The Kinetics of Gaseous Chain Reactions

by

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The recognition of the fact that chain reactions play a widespread rôle in chemical kinetics dates only from some seven years ago. Considerable attention had, of course, been devoted to those few reactions, for example, the photochemical combination of hydrogen and chlorine, in which the phenomenon had first been discovered, but the realisation that formally similar processes go on in so-called thermal reactions, especially in combustion chemistry, opened up a wide field for enquiry in a region of unrelated empiricism. Formerly it appeared impossible that the application of the concepts of kinetics could be applied to such complicated reactions to give even a general description of the nature of the elementary processes constituting these reactions. In many cases, the picture is still far from being complete, and it seems likely to remain so unless new experimental methods be devised, but in the majority of reactions it is now possible to treat the kinetic data to give at least an outline of the nature of the initial, intermediate and final steps in the chain. All this work has led to a closer interrelationship between photo and thermal reactions, the use of photochemical methods aiding considerably and unambiguously in the selection of the correct reaction mechanism.

Perhaps the most important outcome of the theory is the new light it has brought to bear on explosive reactions or rather the conditions necessary for the attainment of explosive

combustion. In a vague way it was believed that the primary cause of explosion was that the heat generated in an exothermic reaction could not escape sufficiently quickly to maintain isothermal conditions in the gas mixture. Semenoff showed, however, in a classical paper published in 1927 dealing with the oxidation of phosphorus, that rapid or explosive reaction may occur if the reaction chains can branch, so giving the reason for the abrupt transition from a practically immeasurable reaction to explosion. At the present time it appears that both ideas are correct - they represent extreme conditions. In practice both factors may be involved in fixing the position of an explosion limit. To determine how far each one need be incorporated in a given reaction it is necessary to study very closely the quantitative relationships between the stable and explosive reactions. This again raises new problems and thereby gives rise to new methods of dealing with them.

Another important line of enquiry comes from the discovery that heterogeneous reactions may induce homogeneous chain reactions, by the evaporation of reactive entities such as radicals from the surface upon which the heterogeneous reaction is occurring. Thus a new class of composite reactions has to be investigated for the phenomenon, as will be seen later, is very specific and so far direct evidence for the existence of this type of reaction very meagre.

The work described in the following papers was done during the later stages of the development of the theory of chain reactions. It was designed to attack some of the problems briefly alluded to above. As it proceeded various ancillary investigations were made with methods developed for dealing with chain reactions, but which were of interest in other branches of chemical kinetics.

The whole scheme of the research is summarised in the diagram which shows the different lines of enquiry pursued during the past four years.

The first investigation[1] was concerned with the effect of foreign gases on the lower explosion limit of phosphorus-oxygen mixtures. In the paper of Semenoff already referred to, the discovery was made that argon facilitated explosion by impeding the loss, by diffusion, of the chain carriers from the gas to the walls. A quantitative theory was developed but when considered more carefully was found to be inadequate, since it became necessary as a result of this work to take into account the different diffusibilities of the chain carriers through the gas mixture. One important result of this was that so-called strong poisons for the oxidation of phosphorus at the upper limit behaved purely as inert gases at the lower limit showing that collisions between carriers and foreign gas under these conditions were elastic. The correction required for taking into account the variation of diffusion coefficient was applied

empirically. In the succeeding paper[5] in this series a theoretical derivation of the corrected equation for the explosion limit was given. In addition an approximate theory for inhibition at the lower limit was proposed and applied to results with lead tetraethyl which was the only substance found to exert a measurable inhibitory action. It is of interest to mention that phosphine was found to have the unique property of raising the lower explosion limit of $P_4 - O_2$ mixtures. After the publication of these papers, several chain reactions were reinvestigated by other workers to see whether the diffusion effect on lower limits was a general phenomenon. The results with phosphorus were confirmed in all the reactions studied. Consequently another paper[6] was written bringing the new data together to show that the theory given in (5) was in agreement with experiment. The inert gas results with phosphine were, however, incomplete and those available appeared to indicate that the inert gas effect was complicated by some form of gas phase inhibition even by such simple gases as argon and nitrogen. A reinvestigation of the PH_3-O_2 reaction was therefore made[21] and it was found that the majority of simple gases were inert and only impeded diffusion, whilst more complicated molecules inhibited the reaction so much that they raised the limit. The inert gas effects were shown to be in agreement with theory, an exact theory of inhibition at the lower limit was worked out in order to be able to calculate inhibition coefficients numerically and a more extensive summary made of inert gas effects from all the available data.

Next an attempt was made to study the oxidation of phosphorus trioxide in the hope that it might prove simpler than that of phosphorus. Various difficulties were encountered and the experiments were finally abandoned. One of the problems was that of making a sensitive direct reading manometer as sensitive as a sulphuric acid U-tube manometer. The construction of this instrument utilising a new principle in this connexion is described in (2).

Another outcome of the work on diffusion is described in (8) and (11). The experiments were mainly carried out with a view to making quantitative a lecture experiment to illustrate the different rates of the interdiffusion of gases. The consistent results obtained with the relatively crude visual method of estimating the depth of colour of bromine vapour suggested that some measurements might be made of the absolute values of the diffusion coefficients to see if they checked with theory. Those results were then further extended by employing a photo-electric cell method of measuring the pressure of the bromine vapour.

Pursuing the main line of investigation the general problems to be considered were (a) the relationship between the kinetics outside of and at the explosion limits to find whether in the oxidation of phosphorus and of phosphine the branching chain theory was quantitatively sufficient to account for the position of both lower and upper limits, (b) the discovery and if possible the detailed analysis of the nature of heterogeneous reactions capable of initiating homogeneous chain processes.

In the theory of the oxidation of phosphorus criteria become evident whereby it is possible to test whether or no a reaction is of the chain type. One of the most useful is the acceleration of rate by inert gases. Thus it is possible to determine if a heterogeneous reaction between two gases, e.g., P_4-O_2 in which chains may be propagated in the gas phase, gives rise to an appreciable number of chain carriers to cause a measurable homogeneous reaction. Upon carrying out experiments[3] with a platinum filament surrounded by a mixture of phosphorus and oxygen at a pressure below the lower limit, all tests for a chain reaction failed. On the other hand with tungsten, molybdenum, glass, evidence of chain propagation was provided not only by the acceleration of the reaction rate with inert gases but also by the appearance of the characteristic green glow. Thus the glow of phosphorus is not necessarily a sign of explosion, it simply indicates a homogeneous reaction between P_4 and O_2. Exact experiments with argan and neon showed that more than 90% of the reaction went on in the gas phase. These experiments also establish the fact that, although in the thermal reaction the number of chains starting per unit time outside the limits is so small as to be immeasurable, yet if artificial means of augmenting this number be introduced a stable reaction is observed having many of the characteristics of the explosion limit itself.

Another method of starting chains is by photochemical excitation. Unfortunately with the phosphorus oxygen reaction, although phosphorus vapour absorbs at a convenient region of the spectrum, there is much doubt about the nature of the products of the reaction. Furthermore it is known that red phosphorus is rapidly deposited so it is difficult to make use of the photo technique to probe further into the mechanism of the reaction. The phosphine-oxygen reaction is, however, very similar as regards general features to that of P_4-O_2. Before a thorough study could be made of the kinetics of the photo oxidation it was necessary to make detailed enquiries[4,7,13] into the nature of the photo-dissociation of the phosphine molecule itself. Such experiments were also of importance since a considerable amount of attention had been devoted to the photochemistry of ammonia and it was desirable to make close comparisons between the behaviour of the two molecules. The mechanism of both the direct and the mercury photo-sensitised decomposition was investigated. During this work a method was devised to show that the low quantum yield (0·5) in the decomposition of phosphine was due to the recombination reaction $PH_2 + H \quad PH_3$. Since the photolysis of ammonia exhibits an abnormally low quantum yield too, the technique used for phosphine was applied to the case of ammonia (12) and again it was shown that a recombination reaction $NH_2 + H$ plays an important part in limiting the extent of the photo-decomposition.

A number of preliminary experiments had been made on the kinetics of the photo-oxidation of phosphine in 4, 7 and 13. These experiments were then extended considerably (9,20) to determine the kinetics in the region outside both explosion limits. One important result of this work was the establishment of the fact that the position of the limits or the condition for explosion is adequately accounted for by the hypothesis of branching chains and that no additional cause for explosion need be introduced into the theory. The phosphine-oxygen explosions are indeed of the true chain type. Another definite conclusion arrived at was that the carrier which reacts with phosphine is an oxygen atom.

Having therefore a fairly detailed knowledge of the chain characteristics of the stable oxidation of phosphine an attempt was made to see if it were possible to initiate chains by means of a hot filament as had proved effective with phosphorus. It was anticipated that some detailed insight might be gained with regard to the nature of the heterogeneous reactions responsible for the ejection of molecules in such a state as to start chains in the gas phase. An extensive study was made of the heterogeneous decomposition of phosphine on tungsten and molybdenum[10] followed by a kinetic analysis of the oxidation[16]. Unfortunately the fraction of homogeneous reaction proved to be so small as to be useless for the purpose outlined above.

The development of the theory of thermal chain reactions had been based almost wholly on kinetic data obtained from the

interaction of combustible molecules with oxygen. The question then arose as to whether nitrous oxide could be substituted for oxygen. One of the most important issues of such a substitution concerned the existence of sharp explosion limits characteristic only of oxidation processes. Nitrous oxide, moreover, possessed a great advantage in that prior to starting this work, the kinetics of its decomposition had been extensively investigated with the result that the first step is the dissociation of an activated molecule into N_2 and O. There was therefore the possibility that the rate of initiation of chains might be accurately calculated, in contrast to the complete lack of knowledge in this respect in all purely thermal chain reactions.

The simplest reaction was that with hydrogen. Preliminary experiments indicated that the reaction went by way of chains, so immediately a scheme was prepared to investigate the kinetics as completely as possible. The first paper[15] describes the results obtained in the thermal high pressure reaction, the second[18] the thermal low pressure reaction and the mercury photosensitised high and low pressure reactions. Since one of the primary objects of this research was the correlation of the behaviour of the hydrogen-oxygen and hydrogen-nitrous oxide reactions a study was made of the effect of small quantities of oxygen on the latter reaction[19]. One of the main conclusions was that as far as stable processes are concerned both reactions exhibit somewhat similar behaviour, but the sharp explosion limits belong wholly to the hydrogen-oxygen reaction. In other

words it is not possible to have branching chains in hydrogen-nitrous oxide mixtures. This is apparently due to the nitrous oxide molecule possessing only one oxygen atom. Chains branch in hydrogen-oxygen reaction on account of the oxygen molecule being diatomic, each of the atoms forming part of a chain carrier. The hydrogen nitrous oxide therefore throws an interesting side light on the nature of the slip in branching chains.

One of the problems which arose in the course of the above investigation was the construction of an intensity filter for the resonance line as 2537 Å of the mercury arc. The construction and uses of this filter are described in (14).

Another problem to which the chain theory seemed likely to contribute some information was the mechanism of polymerisation reactions. The simplest molecule to exhibit this phenomenon is acetylene. A considerable amount of work had already been done on different aspects of this problem, but no exact treatment under the guidance of the chain theory had been given. Such an attack was made using exited mercury atoms as a primary stimulus. The results are briefly discussed in 17, the investigation not yet being quite complete.

Joint Work

All the papers submitted for the degree have been written wholly by the writer, with the exception of the introduction to paper 8. The material in papers 1 and 3 has already been partly used in a thesis for the Ph.D. degree but it is included to show the general scheme of research.

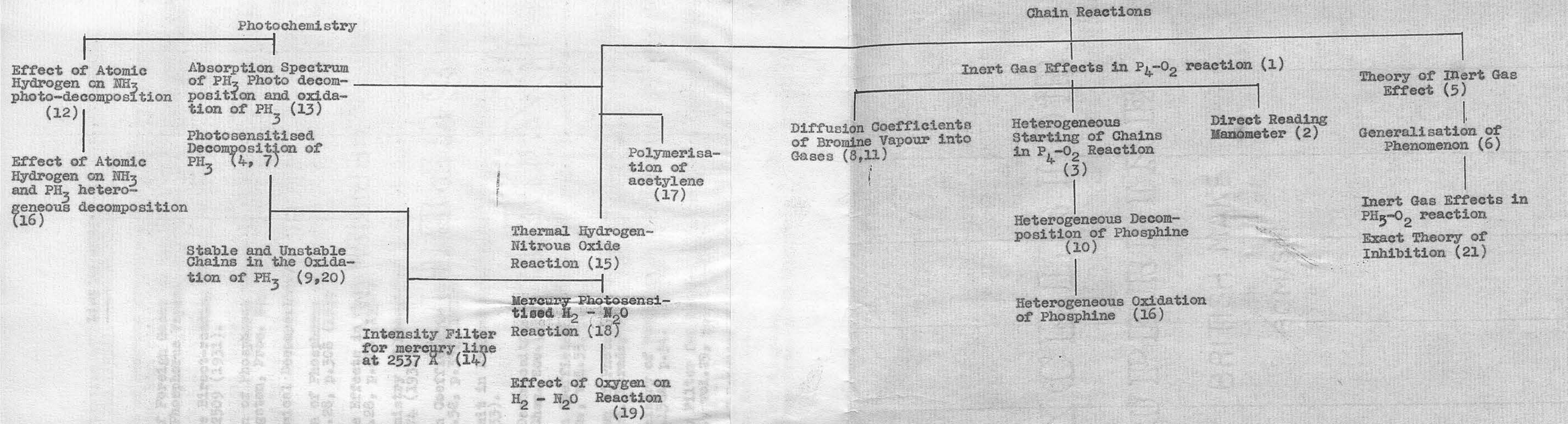
In papers 16, 20 and 21 the experimental work was done by the second author under the direction of the writer. In paper 10 the results for the tungsten filament, described on p.593, were obtained by the second author, and in paper 14 the measurement of the extinction coefficients was made by the second author.

Acknowledgments

The work was mainly carried out in the Chemistry Department of the University of Edinburgh from 1930 to 1933. A small part of it was completed and the experiments on the polymerisation of acetylene made in the laboratory of Colloid Science, University of Cambridge during the early part of 1934.

I should like to place on record my sincere thanks to Dr E.B. Ludlam and Professor J. Kendall for their great encouragement and help during these researches and for the excellent facilities enjoyed in the Edinburgh laboratories. I am also greatly indebted to Professor E.K. Rideal for stimulating discussion on the question of polymerisation reactions, briefly treated in the paper on acetylene.

General Scheme of Research



List of Papers

1. Effect of Foreign Gases on the Lower Critical Oxidation Limit of Phosphorus Vapour, Proc.Roy. Soc., vol.132A, p.108 (1931).

2. Sensitive Direct-reading Mercury Manometer, J. Chem. Soc., p. 2509 (1931).

3. Oxidation of Phosphorus Vapour in Presence of Platinum and Tungsten, Proc. Roy. Soc., vol.135A, p.315 (1932).

4. Photochemical Decomposition of Phosphine, Nature, April 9, 1932.

5. Oxidation of Phosphorus at Low Pressures, Trans, Faraday Soc., vol.28, p.308 (1932).

6. Inert Gas Effects in Chain Reactions., Trans. Faraday Soc., vol.28, p.814 (1932).

7. Photochemistry of Phosphine, I and II, Proc. Roy. Soc., vol.138A, p.374 (1932).

8. Diffusion Coefficients of Bromine Vapour, Proc. Roy. Soc. Edin., vol.52, p.337 (1932).

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10. Thermal Decomposition of Phosphine by Tungsten and Molybdenum, J. Chem. Soc., p.586 (1933).

11. Diffusion Coefficients of Bromine Vapour, II, Proc. Roy. Soc. Edin., vol.53, p.255 (1933).

12. Inhibition of Photo Decomposition of Ammonia by Atomic Hydrogen, Trans. Faraday Soc., vol.28, p.885 (1932).

13. Photochemistry of Phosphine, III and IV, Proc. Roy. Soc., vol.138A, p.541 (1933).

14. Intensity Filter for Mercury Line at 2537 A, Trans. Faraday Soc., vol.29, p.1255 (1933).

15. Kinetics of Reaction between Hydrogen and Nitrous Oxide, I, Proc. Roy. Soc., vol.142A, p.524 (1933).

16. Oxidation of Phosphine in Presence of Tungsten and Molybdenum, J. Chem. Soc., p.264 (1934).

17. Polymerisation of Acetylene, Proc. Roy. Soc., vol.146A, p. 268 (1934).

18. Kinetics of Reaction between Hydrogen and Nitrous Oxide, II, Proc. Roy. Soc., vol.146 A, p.737 (1934).

19. Kinetics of Reaction between Hydrogen and Nitrous Oxide, III, Effect of Oxygen, Proc. Roy. Soc., vol.146A, p.760, (1934).

20. Photochemical Oxidation of Phosphine above the Upper Limit, J. Chem. Physics, vol.2, p.769 (1934).

21. Inert Gas Effects in Phosphine-Oxygen Mixtures, Trans. Faraday Soc., vol.31, p.452 (1935).

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The Effect of Foreign Gases on the Lower Critical Oxidation Limit of Phosphorus Vapour.

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The Effect of Foreign Gases on the Lower Critical Oxidation Limit of Phosphorus Vapour.

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Introduction.

The oxidation of phosphorus has for long been the object of experimental study. It is only within recent years, however, that it has been found possible to apply the laws of chemical kinetics to the problem in order to elucidate its mechanism. This advance was made possible by the study of oxidation of the vapour under carefully regulated conditions. In particular, the experiments of Chariton and Walta,* Semenoff,† and of Kowalski,‡ have established the fact that the luminous oxidation of phosphorus vapour at a given pressure takes place only between two limiting pressures of the reacting oxygen—the lower and upper critical oxidation limits. At pressures less than the lower limit the oxidation is immeasurably slow, whereas at pressures above the upper limit Lord Rayleigh§ has shown that the oxidation is slow and is unaccompanied by luminescence. It was Semenoff who first definitely realised that the mechanism of the luminous oxidation was to be explained on the conception of chain reactions. He therefore applied the theory in a quantitative manner in order to find how the *lower* critical oxidation limit varied with the pressure of the phosphorus vapour, the diameter of the reaction tube, the presence of an inert gas and the temperature of the reaction mixture. The result of his investigation gave the equation

$$p_P p_0 \left(1 + \frac{p_x}{p_0 + p_P}\right) d^2 = \text{constant},$$

where p_0 is the lower critical oxidation pressure, p_P and p_x the pressures of the phosphorus vapour and of the inert gas respectively, d is the diameter of a cylindrical reaction vessel. The " constant " in the equation is independent (within the experimental error) of temperature in the range 0–100° C. Some-

* ' Z. Physik,' vol. 39, p. 547 (1926).
† ' Z. Physik,' vol. 46, p. 109 (1927), also ' Chem. Rev.,' vol. 6 (1929).
‡ ' Z. Phys. Chem.,' vol. 4B, p. 288 (1929).
§ ' Proc. Roy. Soc.,' A, vol. 106, p. 1 (1924).

what later the same equation was deduced by Dalton and Hinshelwood* by a different method but in a more rigorous way, for the oxidation of phosphine at the *lower* critical limit. The method, on account of its generality, is equally suitable for application to the oxidation of phosphorus. In order to derive this equation Semenoff assumed that the reaction chains terminated on the walls of the containing vessel and that the diffusion of the propagators of the chains to the walls was hindered by the presence of an inert gas X. This assumption resulted in the appearance of d^2. For simplicity it was further assumed that the diameters of all molecular species present were equal and that the mean free path in the gas mixture was inversely proportional to the total pressure. The experimental results agreed excellently with the theoretical equation except that they tended to show that the critical oxidation pressure varied inversely as the square root of the pressure of phosphorus vapour. Argon was used as the inert gas.

These assumptions and the resultant theoretical conclusions thus pointed to the probability that the effect of inert gases ought to be entirely independent of their nature. It is the object of this paper to examine more closely this effect: (I) to find out whether the equation is applicable to a wide variety of the common gases and some organic vapours; (II) to compare the results at the lower pressure limit with those at the upper limit which have been obtained by Centnerszwer,† by Tausz and Görlacher and by Schacherl. The interest in the comparison also lies in determining how those substances which are strong poisons or inhibitors for the oxidation at the upper limit behave at the lower limit. In view of the highly specific action of the poisons at the upper limit it was anticipated that with organic vapours at least the effect at the lower limit would also be specific.

Apparatus.

The apparatus used is shown diagrammatically in fig. 1. R is the reaction tube which is immersed in an oil bath which could be heated internally by a resistance wire. For pumping out this is attached to a liquid air trap and a mercury condensation pump backed by a Hyvac oil pump. The oxygen reservoir O with manometer is attached through the several taps and a fine capillary C (obtained by drawing down 1 mm. capillary tube) to R. M is a sulphuric acid manometer read by means of a microscope fitted with an eye-

* 'Proc. Roy. Soc.,' A, vol. 125, p. 294 (1929).

† Centnerszwer, 'Z. Phys. Chem.,' vol. 26, p. 9 (1898); Tausz and Görlacher, 'Z. Anorg. Chem.,' vol. 190, p. 95 (1930); Schacherl, 'Coll. Czech. Chem. Comm.,' vol. 2, p. 665 (1930).

piece scale. P is the vessel containing the white phosphorus, immersed either in a water bath or in melting ice as might be necessary. The foreign gas or

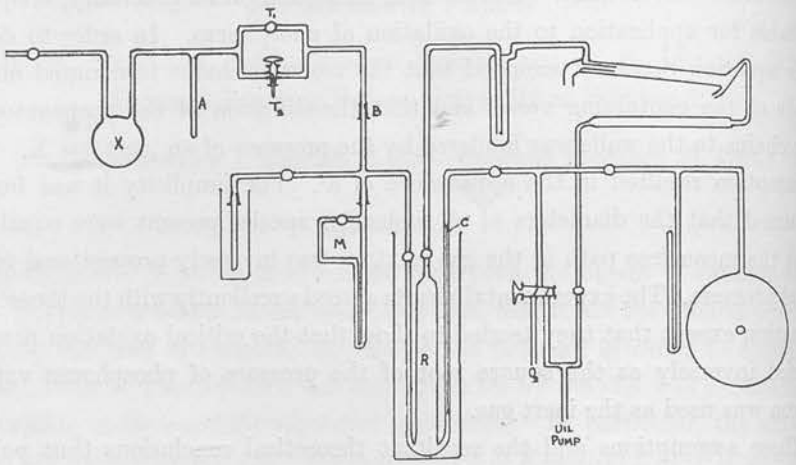

FIG. 1.—Diagram of reaction tube R showing connections to the oxygen reservoir O, to the foreign gas reservoir X and to the phosphorus reservoir P.

vapour is contained in X which is fitted with side tube A and taps T_1 and T_2. T_1 serves for exhausting X while T_2 is made in the form of a small pipette for transferring the gas in X to R in small amounts. When using gases, these were supplied from a small pipette attached to T_3.

Preparation of Materials.

All the organic liquids were obtained in the purest form obtainable; they were fractionally distilled, the middle portion of the distillate being used. The hydrogen was electrolytic and was freed from the residual oxygen by heated palladium asbestos and dried with phosphorus pentoxide. The helium used contained 2 per cent. neon and the neon 2 per cent. helium, while the argon contained 0·5 per cent. nitrogen. Commercial nitrogen (from liquid air) was passed over active heated copper and dried with phosphorus pentoxide as were all the gases used for these experiments. Nitrogen prepared from ammonia and sodium hypobromite solution gave similar results. Carbon monoxide was derived from sodium formate and sulphuric acid. Hydrogen sulphide was prepared from aqueous solution of pure sodium sulphide and dilute sulphuric acid. Nitrous oxide, sulphur dioxide, ethylene and carbon dioxide were obtained from cylinders. Procedure: O was filled with dry oxygen by means of the taps shown. P was detached and a little anhydrous red phos-

phorus introduced. The apparatus was then evacuated and P heated in order to obtain white phosphorus. The white phosphorus prepared in this way was free from oxide. If a gas was being used X was filled as described above. For liquids, a different procedure was adopted. X was detached at the ground joint B, and a small amount of the liquid was run into A. After replacing X, A was then immersed in liquid air and X pumped out. On removing the liquid air and substituting a CO_2/ether, ice or water bath X was filled with vapour at such a pressure that the vapour could easily be admitted to R by means of T_1. In some experiments a portion of the liquid in A was distilled through R to the liquid air trap in order to make sure that the vapour was free from oxygen. This precaution was found to be unnecessary in the later experiments.

With this form of apparatus two methods may be used to determine the critical pressure: (1) observation of the time required for the oxygen to leak into R until a flash indicates that the reaction has occurred: the pressure of oxygen is then calculated from the known rate of flow of oxygen through the capillary under a given pressure in O; (2) by plotting a pressure-time curve for the slow entry of oxygen into R and interpolating for the point of discontinuity: this point is due to the fact that the oxidation of phosphorus vapour results in the formation of an oxide of negligible vapour pressure (*cf.* Semenoff *loc. cit.*). The first method was adopted since it is more accurate than the second and requires only one observation. This latter point was important since about 2000 explosions were required to furnish the data.

Figs. 2 and 3 show respectively the type of curve obtained by plotting explosion times against the pressures of foreign gas and $1/p_0$ against

$$1 + p_x/(p_0 + p_p).$$

These results were obtained with carbon dioxide, the temperature of R being 48°.

The Tables A to H give a few of the results of typical series of experiments. Two different reaction tubes were used during the experiments, the results being correlated by means of experiments carried out with neon. All pressures are in millimetres of mercury.

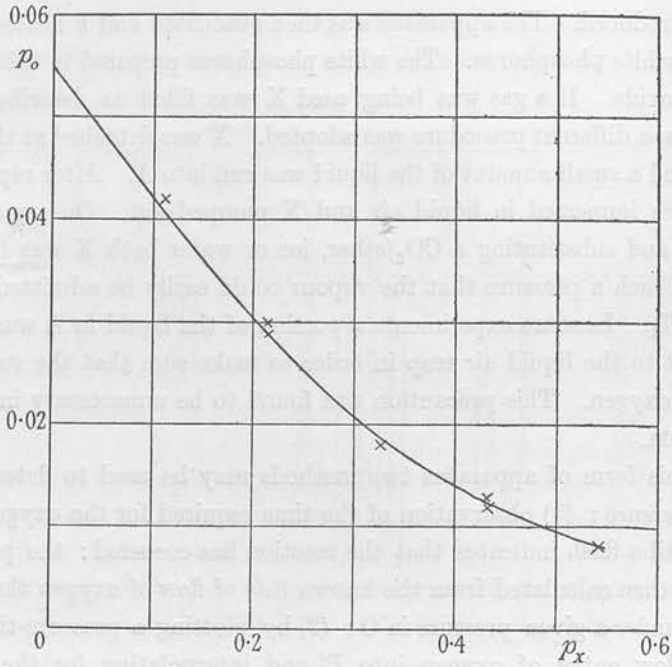

FIG. 2.—Lowering of the critical oxidation pressure (p_0) with increasing pressures (p_x) of the foreign gas, in this case CO_2.

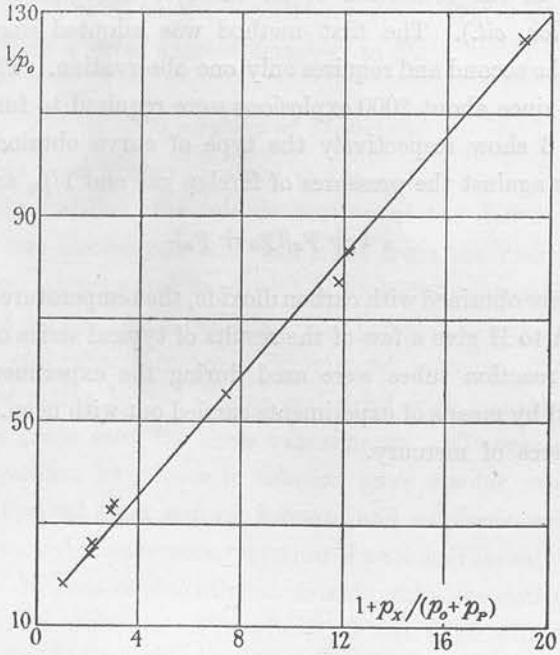

FIG. 3.—Replot of the results of fig. 2, according to Semenoff's equation.

Table A.

Carbon Dioxide.

Temperature of reaction tube 15°.
Temperature of phosphorus 0°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0	0·054	18·5	1·00
0·047	0·032	31	2·3
0·049	0·032	31	2·2
0·097	0·024	41	4·1
0·097	0·024	41	4·1
0·100	0·025	40	4·1
0·108	0·023	44	4·6
0·140	0·017	58	6·7
0·140	0·017	58	6·7
0·162	0·014	72	8·7
0·210	0·009	110	14·1
0·238	0·009	110	15·7
0·243	0·008	125	17·1
0·270	0·006	165	21·7

Nitrogen.

Temperature of reaction tube 15°.
Temperature of phosphorus 0°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0	0·054	18·5	1·00
0·059	0·035	29	2·4
0·068	0·035	29	2·6
0·135	0·023	43	5·5
0·135	0·027	37	5·0
0·170	0·022	46	6·9
0·175	0·020	50	7·5
0·211	0·016	64	10·2
0·211	0·016	64	10·2
0·216	0·016	64	10·2
0·216	0·016	64	10·2
0·243	0·012	84	13·8
0·248	0·014	74	12·8
0·251	0·012	81	14·2
0·251	0·014	74	13·0
0·292	0·009	110	19·2

Table B.

Nitrous Oxide.

Temperature of reaction tube 15°.
Temperature of phosphorus 0°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0	0·054	18·5	1·00
0·051	0·033	31	2·3
0·054	0·034	30	2·3
0·054	0·034	30	2·3
0·108	0·022	45	4·7
0·108	0·023	43	4·6
0·108	0·021	47	4·8
0·162	0·014	71	8·7
0·162	0·015	66	8·4
0·216	0·011	88	12·8
0·216	0·011	88	12·8
0·218	0·011	88	13·0
0·278	0·008	125	19·6

Ethylene.

Temperature of reaction tube 15°.
Temperature of phosphorus 0°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0	0·054	18·5	1·00
0·076	0·032	31	2·9
0·076	0·035	29	2·8
0·081	0·036	28	2·9
0·138	0·024	41	5·4
0·140	0·021	49	6·1
0·143	0·024	42	5·6
0·208	0·017	60	9·8
0·216	0·016	64	10·5
0·216	0·017	60	10·1
0·224	0·015	66	11·0
0·292	0·011	93	17·4
0·305	0·010	100	18·6
0·305	0·010	100	18·6

Table C.

Neon.

Temperature of reaction tube 15°.
Temperature of phosphorus 0°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0	0·054	18·5	1·00
0·035	0·045	22	1·7
0·086	0·038	26	2·9
0·092	0·038	26	3·0
0·092	0·037	27	3·1
0·143	0·031	33	4·8
0·194	0·026	38	6·7
0·197	0·030	33	6·3
0·189	0·030	33	6·1
0·192	0·027	36	6·5
0·248	0·024	42	9·0
0·268	0·023	44	10·0
0·292	0·021	49	11·2
0·296	0·021	49	11·8
0·389	0·012	81	21·0

Hydrogen.

Temperature of reaction tube 15°.
Temperature of phosphorus 15°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0	0·068	14·7	1·00
0·086	0·064	15·8	1·98
0·103	0·061	16·4	2·2
0·175	0·057	17·6	3·1
0·175	0·058	17·2	3·1
0·189	0·054	18·5	3·4
0·257	0·049	20	5·0
0·257	0·054	18·5	4·3
0·270	0·049	20	4·7
0·346	0·047	21	6·6
0·432	0·043	23	7·4
0·460	0·042	24	7·9
0·540	0·040	25	9·3
0·568	0·037	27	10·2

Table D.

Argon.

Temperature of reaction tube 15°.
Temperature of phosphorus 15°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0	0·068	14·7	1·00
0·051	0·055	18·2	1·64
0·057	0·046	22	1·80
0·076	0·043	23	2·12
0·111	0·044	23	2·6
0·135	0·040	25	3·1
0·184	0·029	34	4·4
0·194	0·027	37	4·7
0·219	0·026	38	5·3
0·275	0·022	45	6·9
0·319	0·018	55	8·4
0·342	0·017	62	9·3
0·365	0·014	71	10·4
0·405	0·013	77	11·7
0·435	0·012	83	12·8
0·460	0·011	91	13·8
0·485	0·010	100	14·9

Helium.

Temperature of reaction tube 15°.
Temperature of phosphorus 15°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0	0·068	14·7	1·00
0·095	0·057	17·5	2·53
0·102	0·056	17·9	2·67
0·186	0·054	18·5	3·35
0·240	0·048	21	4·3
0·243	0·049	20	4·3
0·281	0·045	22	5·0
0·289	0·045	22	5·1
0·324	0·041	24	5·9
0·356	0·041	24	6·4
0·391	0·040	24	6·8
0·405	0·038	26	7·4
0·508	0·034	29	9·6
0·516	0·035	29	9·6
0·590	0·031	32	11·5
0·652	0·028	36	13·3

Table E.

Acetone.

Temperature of reaction tube 15°.
Temperature of phosphorus 15°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0	0·068	14·7	1·00
0·032	0·053	18·9	1·41
0·049	0·043	23	1·72
0·068	0·042	24	2·01
0·078	0·034	29	2·32
0·095	0·028	36	2·79
0·097	0·025	40	2·94
0·121	0·023	43	3·5
0·130	0·022	45	3·8
0·135	0·019	53	4·1
0·156	0·018	56	4·6
0·175	0·018	56	5·1

Acetone slowly dissolved in the sulphuric acid in the manometer. Prolonged pumping was necessary after each experiment.

Mesitylene.

Temperature of reaction tube 15°.
Temperature of phosphorus 15°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0	0·068	14·7	1·00
0·038	0·054	18·5	1·48
0·065	0·045	22	1·93
0·076	0·037	27	2·2
0·081	0·033	30	2·4
0·095	0·033	30	2·6
0·111	0·028	36	3·1
0·127	0·026	39	3·5
0·132	0·025	40	3·6
0·146	0·018	56	4·4
0·162	0·015	67	5·1
0·170	0·013	77	5·5
0·189	0·012	83	6·1
0·200	0·013	77	6·3
0·216	0·011	90	7·0
0·243	0·009	110	8·2

Table F.

Methylene Chloride.

Temperature of reaction tube 15°.
Temperature of phosphorus 15°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0	0·068	14·7	1·00
0·027	0·055	18·2	1·45
0·030	0·053	18·9	1·39
0·054	0·041	24	1·82
0·070	0·032	31	2·2
0·081	0·034	29	2·4
0·089	0·026	38	2·7
0·097	0·029	34	2·8
0·105	0·022	45	3·4
0·119	0·019	53	3·7
0·135	0·017	59	4·2
0·162	0·014	71	5·2
0·170	0·013	77	5·5
0·197	0·011	91	6·5
0·216	0·009	110	7·4
0·219	0·008	120	7·6

Benzene.

Temperature of reaction tube 15°.
Temperature of phosphorus 15°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0	0·068	14·7	1·00
0·048	0·046	22	1·68
0·054	0·040	25	1·83
0·070	0·037	27	2·13
0·089	0·028	36	2·68
0·108	0·027	37	3·1
0·135	0·022	45	3·9
0·176	0·018	56	5·1
0·189	0·016	62	5·6
0·257	0·011	91	8·1
0·237	0·012	83	7·9
0·270	0·009	110	9·0
0·351	0·008	130	11·7
0·405	0·005	200	14·5
0·432	0·005	200	15·4

Table G.

Hexane.
Temperature of reaction tube 15°.
Temperature of phosphorus 15°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0	0·068	14·7	1·00
0·030	0·053	18·9	1·38
0·032	0·051	19·6	1·42
0·046	0·050	20·0	1·61
0·054	0·046	22	1·76
0·073	0·041	24	2·1
0·081	0·034	29	2·4
0·092	0·033	30	2·6
0·105	0·026	39	3·1
0·108	0·026	39	3·1
0·135	0·022	45	3·9
0·135	0·019	53	4·1
0·159	0·018	56	4·7
0·162	0·017	59	4·9
0·211	0·014	71	6·4
0·270	0·009	110	9·0

Hydrogen Sulphide.
Temperature of reaction tube 15°.
Temperature of phosphorus 15°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0	0·068	14·7	1·00
0·051	0·051	19·6	1·67
0·054	0·053	18·9	1·69
0·095	0·041	24	2·4
0·143	0·027	37	3·8
0·149	0·027	37	3·9
0·195.	0·018	56	5·5
0·197	0·019	53	5·5
0·243	0·016	63	6·9
0·243	0·016	63	6·9
0·320	0·008	125	10·7
0·324	0·008	125	10·8
0·410	0·004	250	15·1

Table H.

Sulphur Dioxide.
Temperature of reaction tube 15°.
Temperature of phosphorus 15°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0	0·068	14·7	1·00
0·041	0·048	21	1·55
0·068	0·046	22	1·96
0·081	0·039	26	2·3
0·108	0·040	25	2·7
0·156	0·027	37	4·0
0·192	0·026	38	4·8
0·230	0·022	45	5·9
0·238	0·021	48	6·2
0·272	0·017	59	7·5
0·300	0·016	63	8·3
0·349	0·014	71	9·9
0·378	0·012	83	11·2
0·432	0·011	91	13·0
0·513	0·009	110	16·1
0·580	0·008	125	18·6

Acetylene.
Temperature of reaction tube 15°.
Temperature of phosphorus 15°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0	0·068	14·7	1·00
0·046	0·057	17·5	1·56
0·049	0·054	18·5	1·60
0·057	0·051	19·7	1·75
0·076	0·049	20	2·0
0·108	0·044	23	2·6
0·154	0·040	25	3·4
0·167	0·035	29	3·8
0·186	0·034	29	4·2
0·216	0·030	34	4·9
0·257	0·027	37	5·9
0·292	0·022	46	7·3
0·324	0·020	49	8·2
0·378	0·018	57	9·9
0·397	0·014	70	10·2

Discussion.

The foregoing results are summarised in fig. 4, where the reciprocal of the critical oxygen pressure is plotted against the quantity $1 + p_x/(p_0 + p_P)$. The first point to be noted is that this equation is applicable to all gases and vapours used in these experiments. The effect of the following substances can also be expressed by the same equation (for brevity the actual figures are not given): Carbon tetrachloride, chloroform, carbon disulphide, carbon monoxide, nitrobenzene, phosphorus trichloride, phosphorus tribromide and phosphorus oxychloride. The slopes of the curves obtained are not identical as would be anticipated on Semenoff's theory, but vary between the extremes hydrogen 0·134 and mesitylene 1·30—a variation which is much greater than could be accommodated in the approximate theory of the effect.

Two possible explanations might be advanced to explain this wide variation: (1) that in addition to preventing the chains from reaching the walls of the vessel by decreasing the mean free path, the foreign gas is capable of destroying or deactivating the propagators of the reaction chain, the efficiency of the deactivation being specific for each gas; (2) that the foreign gas forms a film on the surface of the reaction tube which has a specific power of stopping or of reflecting the chains. In this connection mention may be made of the difficulty experienced by Dalton and Hinshelwood (*loc. cit.*) in obtaining reproducible surface conditions in the low pressure oxidation of phosphine.

Dealing with (2) first of all, the following points definitely prove this explanation untenable. In the first place, the variation in the slopes of the curves for hydrogen, helium, neon and argon are much too large to be explained in this way. Secondly, experiments were made with tubes, of which the surfaces were (1) clean, (2) covered with phosphorus pentoxide, (3) with paraffin wax, (4) with platinised glass; the slopes of the curves were found to be independent of the nature of the surface of the reaction tube. Further, any modification of the equation proposed by Semenoff to take into account the adsorption of a film on the surface of the reaction tube resulted in equations which did not fit the experimental results.

The objection to the first explanation is not so strong. It is, however, to be observed that in fig. 4 the heavy and large organic molecules give curves with the greatest slopes, *i.e.*, prevent the diffusion of the chains to the walls to the greatest extent, the common gases occupy an intermediate position with a tendency for the heavier molecules to have greater slopes; the lighter molecules or atoms H_2, He, Ne, are arranged in order of their masses with

hydrogen much nearer to helium than would be expected if mass operated alone. The effect thus seemed to depend more on the *physical* properties of

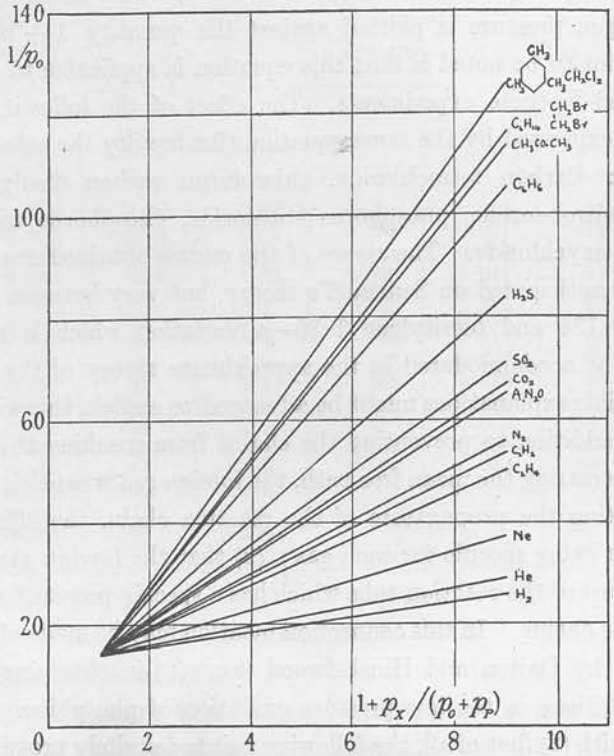

FIG. 4.—Variation of A with the nature of the foreign gas. A is the slope of the line obtained by plotting $1/p_0$ against $\left(1 + \frac{p_x}{p_0 + p_p}\right)$ p_0, p_x and p_p being the critical oxidation pressure, the pressure of foreign gas and the pressure of phosphorus respectively.

the gas rather than on a chemical property which is usually more specific in character. The obvious physical property which might determine the order in the above series of gases is the *diffusion coefficient*.

The difficulty lay in the introduction of the diffusion coefficient into the existing theory without modifying Semenoff's equation to any great extent. The rigorous theory has been attempted by Semenoff* for the chain reaction between hydrogen and oxygen, but the resulting equation is so complicated and contains so many unmeasurable factors that much simplification had to be carried out before it would fit the experimental data. The reaction between

* 'Z. Phys. Chem.,' B, vol. 2, p. 161 (1929).

phosphorus vapour and oxygen is even more complicated so that there seems at present little hope of solving the problem in this manner. Nevertheless, the arrangement of the slopes of the curves suggested that the existing equation could be preserved and brought into harmony with the data most simply by multiplying p_x by a diffusion coefficient characteristic of X. The formula which has been found to represent most satisfactorily the diffusion of one gas into another is that based on the Stefan-Maxwell theory of diffusion (Jeans, "Dynamical Theory of Gases," p. 315). It is given by the equation

$$D_{12} = \frac{K}{S_{12}^2} \sqrt{\frac{1}{M_1} + \frac{1}{M_2}},$$

where D_{12} is the diffusion coefficient of gas 1 into gas 2. K is a constant which is a function of the temperature. S_{12} is the sum of the molecular diameters of 1 and 2 with molecular weights respectively M_1 and M_2. Let M_2 be the molecular weight of the foreign gas, the problem then is to determine the mass and diameter of gas 1. In the theory of chain reactions (see Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," 2nd ed., p. 173) two energy rich propagators are assumed to take part in the chain—the activated product X_p which loses, by collision, wholly or partly its energy to form the activated reactant X_0. Hence in order to estimate the diffusibility of X_0 and X_p through 2 it is necessary to know their masses and effective diameters. In the case of the phosphorus oxidation X_0 may either be an oxygen atom or an activated oxygen molecule capable of surviving the collisions with inert gas molecules while X_p is probably a phosphorus oxide molecule which may be represented by the general formula P_4O_n where n varies from 1 to 10. In comparison with X_0, X_p will therefore be a comparatively slow diffuser owing to its mass and large diameter. As a first approximation it is neglected in what follows. [Assuming that $P_4O_n = P_4O_5$ as a mean and using a probable value for the molecular diameter, it was found that D for P_4O_5 is small compared with and varies approximately with D_{12}, so that the general character of the results tabulated below remains unchanged.] Table I shows the result of multiplying the slopes of the curves in fig. 4 by the diffusion coefficient for oxygen atom and oxygen molecule respectively. As a basis for calculation the diameter of the oxygen atom was taken to be equal to that of neon, while for the oxygen molecule the kinetic theory value has been taken. The values for molecular diameters have been taken from the Landolt-Börnstein ' Tabellen.'

Table I.

Gas.	Slope = A.	Oxygen atom.		Oxygen molecule.	
		D_{12}.	$D_{12} \times A$.	D_{12}.	$D_{12} \times A$.
Hydrogen	0·134	1·00	1·0	1·00	1·0
Helium	0·169	0·90	1·2	0·85	1·0
Neon	0·264	0·45	0·9	0·37	0·7
Ethylene	0·42	0·25	0·8	0·23	0·7
Acetylene	0·46	0·25	0·9	0·23	0·7
Nitrogen	0·48	0·26	0·9	0·23	0·7
Nitrous oxide	0·60	0·18	0·8	0·23	1·0
Argon	0·60	0·27	1·3	0·27	1·1
Carbon dioxide	0·62	0·18	0·8	0·23	1·0

The values of D_{12} for the atom and for the molecule and of $D_{12} \times A$ are given relative to hydrogen which is taken as unity in all cases.

Since molecular diameters for some of the gases and vapours used were not available the calculation of D_{12} was carried out by a method which is detailed by J. H. Arnold.* It is assumed that S_{12} is proportional to $(V_1^{1/3} + V_2^{1/3})$ where V_1 and V_2 are the molecular volumes of 1 and 2 (in the liquid state) at corresponding temperatures. Since V_1 is unknown for the oxygen atom the following Table (II) has been compiled for the oxygen molecule only. The values of V_2 are taken from Le Bas, "Molecular Volumes of Liquid Chemical Compounds." The diffusion equation thus becomes

$$D_{12} = K' (V_1^{1/3} + V_2^{1/3})^{-2} \sqrt{\frac{1}{M_1} + \frac{1}{M_2}},$$

where K′ is another constant.

Table II.

Gas.	Slope = A.	$D_{12} \times A$.
Benzene	1·06	1·0
Hexane	1·20	1·0
Methylene chloride	1·30	1·3
Mesitylene	1·30	1·0
Ethylene dibromide	1·20	1·0
Acetone	1·16	1·3
Hydrogen sulphide	0·81	1·0
Sulphur dioxide	0·67	0·9

The values of $D_{12} \times A$ are referred to benzene which is taken as unity.

* "Industrial and Engineering Chemistry," vol. 22, p. 1091 (1930).

The agreement obtained by multiplying A by D_{12}, although by no means exact, is sufficient to show that the effect is dominated by D_{12}. The results in Table I also show that it is difficult to decide between the atom and the molecule for X_0.

The variations which are apparent are, no doubt, due to several factors; probably to small specific effects of the foreign gas, to the difficulty of knowing the physical constants of X_0 and in no small degree to the uncertainty as to the effective molecular diameters in the collisions between X_0 and X. The neglect of X_p also contributes to the error. Further progress towards better agreement is thus hindered by the lack of knowledge of the mechanism of the reaction and by the difficulty, when applying the kinetic theory, of obtaining reasonably simple equations amenable to experimental investigation.

Additional support for the supposition that the diffusion factor is predominant is afforded by an examination of the temperature coefficient of A. The diffusion coefficient is proportional to $T^{3/2}/1 + \frac{c}{T}$ where T is the absolute temperature and C is Sutherland's constant for the system in question and is given by the Sutherland formula $C = F\sqrt{C_1 . C_2}$ where C_1 and C_2 are the individual Sutherland constants for the two gases, F is a factor not differing far from unity provided the molecular volumes of the two gases are not greatly different (*cf.* Arnold, *loc. cit.*). From this it would be expected that A would be given by

$$A = k\,(1 + C/T)\,T^{-3/2},$$

where k is a constant.

In order to test this equation three gases were selected—neon, carbon dioxide and ethylene. Ethylene was chosen since it was anticipated that at higher temperatures it would exert a poisoning action in addition to the normal increase in diffusion coefficient. As has been shown by Semenoff, and confirmed in the experiments to be described, temperatures from 0° to 100° C. have no measurable effect on the lower critical oxidation pressure. This fortunate circumstance allowed a direct test of the above equation, obviating the necessity of applying any additional corrections.

A few of the results for neon and for ethylene are given in Tables III and IV. The results for carbon dioxide are summarised in Table V. For brevity, they are not given *in extenso*.

Table III.

Neon : Temperature of phosphorus 0°. Critical pressure 0·054 mm.

Temperature of reaction tube 15°. Temperature of reaction tube 112°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.	p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0·035	0·045	22	1·9	0·074	0·044	23	2·5
0·086	0·038	26	2·9	0·081	0·045	22	2·6
0·143	0·031	33	4·8	0·170	0·039	26	4·6
0·194	0·027	38	6·7	0·181	0·038	26	5·0
0·248	0·024	42	9·0	0·265	0·033	30	7·6
0·292	0·021	49	11·2	0·270	0·031	32	8·1
0·389	0·012	80	21	0·351	0·027	37	11·3
				0·440	0·022	46	16·2

Temperature of reaction tube 60°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0·084	0·044	23	2·7
0·138	0·039	26	4·0
0·140	0·038	26	4·1
0·189	0·035	29	5·5
0·189	0·035	29	5·5
0·240	0·030	33	7·5
0·246	0·028	36	8·0
0·348	0·021	48	13·4
0·378	0·023	44	13·6

Table IV.

Ethylene : Temperature of phosphorus 0° C.

Temperature of reaction tube 14°. Temperature of reaction tube 23°.

p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.	p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0	0·054	18·5	1·00	0	0·054	18·5	1·00
0·081	0·036	28	2·88	0·054	0·034	29	2·32
0·157	0·023	44	6·2	0·100	0·026	39	4·0
0·218	0·017	59	10·1	0·100	0·027	37	3·9
0·224	0·015	67	11·2	0·159	0·021	48	6·7
0·290	0·010	100	18	0·211	0·008	125	15
0·305	0·010	100	19	0·211	0·009	90	14
0·378	0·008	125	26	0·270	0·006	165	22

Table IV—(continued).

Temperature of reaction tube 70°.				Temperature of reaction tube 116°.			
p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.	p_x.	p_0.	$1/p_0$.	$1+\frac{p_x}{p_0+p_P}$.
0	0·054	18·5	1·00	0	0·054	18·5	1·00
0·103	0·037	27	3·34	0·054	0·043	23·1	2·08
0·108	0·032	31	3·77	0·108	0·038	26	3·4
0·162	0·025	40	6·1	0·108	0·038	26	3·4
0·162	0·026	39	5·9	0·170	0·032	31	5·4
0·216	0·021	48	8·7	0·237	0·029	35	7·2
0·267	0·017	59	11·8	0·291	0·025	40	10·1
0·270	0·018	56	11·4	0·297	0·025	40	10·3
				0·351	0·022	45	11·1

Table V.

Neon.			Ethylene.			Carbon Dioxide.		
T.	A.	$\frac{T^{3/2}}{1+c/T}\times A$.	T.	A.	$\frac{T^{3/2}}{1+c/T}\times A$	T.	A.	$\frac{T^{3/2}}{1+c/T}\times A$.
285	0·26	102	287	0·42	130	324	0·56	210
334	0·22	106	296	0·36	120	354	0·50	230
385	0·17	102	343	0·27	120	383	0·43	220
			389	0·19	102			

The values of the Sutherland constants were obtained from the recent results of Trautz and Zink, ' Ann. Physik,' vol. 7, p. 427 (1930).

The comparison of the above results with these obtained at the upper limit by Centnerszwer and more recently by Tausz and Görlacher and by Schacherl show very striking divergences. Tausz and Görlacher found that their results could be represented by the equation

$$p_x = K/(a + x),$$

p_x = pressure of oxygen above which the luminous oxidation is arrested and x is the percentage (by volume) of the foreign gas. The value of 1/K was taken as a measure of the activity of the poison. For the common gases it was found that they had little effect on p_x. Centnerszwer, however, found that under his experimental conditions the gases N_2, CO, CO_2, H_2 and N_2O exerted a small but measurable effect in reducing p_x. This is in marked contrast with the low pressure experiments in which the effect of carbon dioxide is four times greater than that of hydrogen. Sulphur dioxide is, according

to Tausz and Görlacher, a feeble poison of about the same efficiency as benzene, whereas the value of A for SO_2 is only slightly greater than that for CO_2, and is much smaller than A for benzene. Again, benzene exerts a poisoning effect six times as great as that of ethylene dibromide (Centnerszwer), while A for benzene is 1·06 and for ethylene dibromide 1·20. It is unnecessary to amplify these comparisons, which show very clearly the differences which exist at the two oxidation limits.

The behaviour of ethylene may be examined rather more closely on account of the results obtained at different temperatures. This gas has a value of 1/K which is 10 times that of SO_2, and has therefore been regarded for a considerable time as a fairly strong inhibitor of the glow of phosphorus. At the lower limit it assumes its normal position, lying close to acetylene and nitrogen. This result, therefore, points to the conclusion that collisions between X_0 and ethylene molecules are for the most part elastic, up to pressures where the ethylene concentration is 10 times that of oxygen. Ethylene appears to behave abnormally at temperatures above 20° C. as the value of A decreases by a greater amount than can be accounted for by the increase in the diffusion coefficient. If the assumption is made that this abnormal decrease is due to the destruction of X_0 in the gas phase by ethylene and that this reaction has a temperature coefficient, it is possible, on the basis of a theory advanced by Kowalski, to make a very rough estimate of the efficiency of the collisions between X_0 and ethylene resulting in the destruction of X_0.

Kowalski showed that the rate (w) of the oxidation of phosphorus vapour is given by

$$w = \frac{p_0}{1/\nu - a + \dfrac{p_x}{p_x + p_P}}, \qquad (1)$$

where n_0 is number of primary reactions occurring in 1 second, ν is proportional to the length of the chains, a is a constant within the temperature range at present being considered, p_x is the partial pressure of a poison and $p_x/(p_x + p_P)$ is the probability of a collision between X_0 and poison. In order to take into account the temperature coefficient (1) will assume the form

$$w = \frac{n_0}{1/\nu - a + \dfrac{p_x}{p_x + p_P} e^{-U/RT}}, \qquad (2)$$

where $e^{-U/RT}$ is the ratio of the number of effective collisions to the total number of collisions, U being the energy of activation.

For condition of explosion $w = \infty$, therefore

$$1/\nu - a + \frac{p_x}{p_x + p_P}\, e^{-U/RT} = 0. \tag{3}$$

But Semenoff has shown that

$$\nu = \frac{6\pi d^2}{4\lambda_0^2}\, p_0 p_P \left(1 + \frac{p_x}{p_0 + p_P}\right), \tag{4}$$

which may be modified to allow for the differences in diffusion coefficient by writing it in the form

$$\nu = \frac{6\pi d^2}{4\lambda_0^2}\, p_0 p_P \left(1 + \frac{D p_x}{p_0 + p_P}\right), \tag{4'}$$

where λ_0 is the mean free path at unit pressure. Let $4\lambda_0^2/6\pi d^2 = K$, then substituting (4') in (3) and as an approximation taking $p_x/(p_x + p_P)$ equal to unity ($p_P = 0{\cdot}007$ mm. and p_x ranged up to $0{\cdot}4$ mm.)

$$\frac{K}{a} = p_0 p_P \left(1 + \frac{D p_x}{p_0 + p_P}\right)(1 - 1/a\, e^{-U/RT}), \tag{5}$$

or if

$$A' = \frac{1/p_0}{1 + D p_x/(p_0 + p_P)},$$

$$\frac{K}{a p_P} . A' = 1 - 1/a\, e^{-U/RT},$$

i.e.,

$$\frac{d \ln A'}{dT} = -\frac{U}{RT^2}.$$

For the 100° range $A'_1/A'_2 \doteqdot 1{\cdot}5$, so that $U \doteqdot 10^3$ cals. and therefore it would appear that only one collision in 5 is effective in destruction of X_0 at a temperature of 80° C.

These comparisons thus show that there is no correlation between the effect of foreign gases and vapours at the higher and at the lower critical oxidation limits of phosphorus vapour. This is in keeping with the theories which have already been proposed for the mechanism of the reaction. At the upper limit the length of the reaction chains is determined solely by deactivation or destruction of the propagators in the gas phase, whereas at the lower limit the chain length is governed by the facility with which the propagators may reach the wall of the containing vessel where they are destroyed or transformed in some way which is as yet uncertain.

In conclusion, we wish to express our thanks to Professor Kendall

for continued interest and encouragement, to the Imperial Chemical Industries, Ltd., for a grant for apparatus and to the Carnegie Trustees whose scheme for the endowment of research enabled the work to be undertaken.

Summary.

The effect of different gases and vapours on the lower critical oxidation limit of phosphorus vapour has been investigated in order to test the equation originally proposed by Semenoff.

It has been found that although the equation represents the results satisfactorily, the slope of the curve obtained by plotting the reciprocal of the critical oxidation pressure against the quantity $\left(1 + \frac{p_x}{p_0 + p_P}\right)$ depends on the nature of the gas. (p_x, p_P, p_0 are the pressures of foreign gas, phosphorus and oxygen.)

From the results obtained it is concluded, in the present approximate state of the theory, that the differences are to be explained on the variation of the diffusion coefficient (D) of the chain propagators into the foreign gas. Empirically the equation is modified to

$$p_0\, p_P\left(1 + \frac{Dp_x}{p_0 + p_P}\right) = \text{constant.}$$

The results therefore show no correlation with those obtained for foreign gases at the upper critical oxidation limit.

Evidence from the variation of the slopes of the curves with temperature confirms the opinion that variation of the *diffusion coefficient* is the predominating cause of the differences obtained.

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Reprinted from the Journal of the Chemical Society, 1931.

CCCXLIV.—*A Sensitive Direct-reading Mercury Manometer.*

By Harry W. Melville.

ring the course of an investigation of the oxidation of phosorus trioxide vapour at low pressures, a direct-reading manometer s required which was sensitive to at least 0·001 mm. of mercury. ice the use of the simple **U**-tube manometer employing oil or lphuric acid was precluded owing to the solubility of the phosorus trioxide in these liquids, a manometer was devised employ- a principle which, it is believed, has not been previously used this connexion.

The manometer consists essentially of a small inverted glass p (*C*) floating in mercury as shown in Fig. 1. The simple theory as follows. Let the pressures of gas on the outside and inside of e cup be identical; the cup will then sink into the mercury until e weight of liquid displaced is equal to the weight of the cup. If ie pressure is now increased on the outside of the cup by Δp the tal force exerted downwards on the cup is proportional to $\pi r^2 . \Delta p$, here r is the radius of the cup. This will result in the cup sinking rther into the mercury by a distance Δx,* the weight of mercury splaced being equal to $\Delta x . 2\pi rt\rho$, where t is the thickness of the p and ρ the density of mercury. For equilibrium, then,

$$\Delta p . \pi r^2 = K . \Delta x . 2\pi rt\rho,$$

here K is a constant depending only on the units used to express p. The sensitivity $\Delta x/\Delta p$ is thus given by $\Delta x/\Delta p = r/2Kt\rho$, and order to make this large, r must be large and t small. Calculation owed that if $r = 1$ cm., $t = 10^{-2}$ cm., and the smallest value of x which can be detected is 10^{-3} cm. (by means of a microscope tted with an eye-piece scale), the required sensitivity could be eached.

Two different forms of the manometer were constructed as shown n Figs. 1 and 2. They differed only in the arrangement of the uides for the cup. The glass cups were made from 1 cm. tube by rawing and blowing it simultaneously. The tubing was then cut nto convenient lengths by covering the selected parts with paraffin ax, drawing a furrow in the wax with a fine steel point, and tching through with hydrofluoric acid. For practical purposes, he limit to the thickness was about 10^{-2} cm.: cups were made

* In addition the levels of the mercury outside and inside the cup change ut this motion is small compared with the motion of the cup in this particular case and is therefore neglected in the simple theory.

with $t = 5 \times 10^{-3}$ cm. or less, but they were rather fragi
were easily broken when being attached to their guide rods
cup was attached to the glass rod (R) as shown in Fig. 1.
lower end of the rod a small tube (M) filled with mercur
fused on in order to sink the cup well into the mercury and
the centre of mass of the floating system below the surface
mercury. This tube moved in a glass guide, and a guide
platinum wire or foil served at the upper end of the rod.
large ground joint facilitated the adjustment and removal
cup, and the tap allowed the manometer to be used differenti

The second design is shown in Fig. 2. In this case the cu

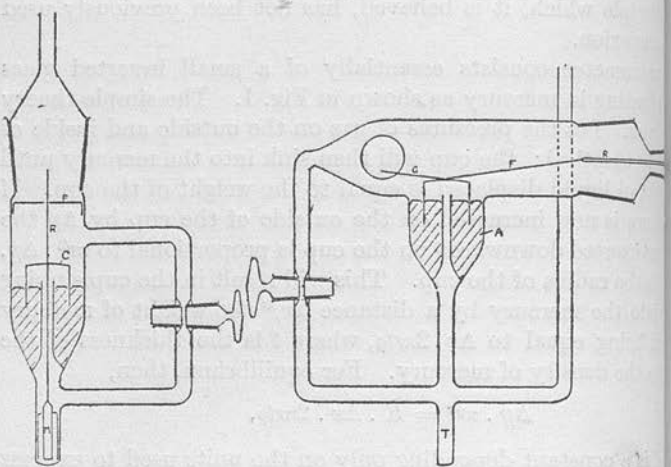

FIG. 1. FIG. 2.

supported by two thin glass fibres (F) so that vertical m
could easily take place, whereas horizontal movement was prev
These were attached to a glass rod (R), which in turn was fu
one half of a ground joint as shown. The large joint was nec
for the insertion and removal of the cup. The small join
made slightly eccentric with respect to the large one so that th
could be accurately adjusted when the manometer was evac
The motion of the cup was observed by means of a fine
pointer (G). A considerable magnification of the motion o
obtained by making the pointer much longer than the supp
fibres. The side tube (T) prevented the blocking of the
leading to the apparatus in the event of mercury being force
of A by sudden pressure changes in the apparatus.

Although the manometer in Fig. 2 is not quite so compa
that in Fig. 1, the absence of glass and metal guides elimin

large extent any tendency to stick. During experiments with anometer 2 the highest sensitivity reached was 2×10^{-4} mm. of ercury. An attempt was made to increase this still further by placing the mercury by concentrated sulphuric acid (compare pression for $\Delta x/\Delta p$), but there was no increase in sensitivity, owing that the limit was governed by the elasticity of the pporting fibres.

UNIVERSITY OF EDINBURGH. [*Received, May 16th*, 1931.]

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The Oxidation of Phosphorus Vapour at Low Pressures in Presence of Platinum and Tungsten.

BY H. W. MELVILLE AND E. B. LUDLAM.

[*Reprinted from the* PROCEEDINGS OF THE ROYAL SOCIETY, A, Vol. 135.]

The Oxidation of Phosphorus Vapour at Low Pressures in Presence of Platinum and Tungsten.

By H. W. MELVILLE, Carnegie Scholar, and E. B. LUDLAM, Carnegie Teaching Fellow.

(Communicated by J. Kendall, F.R.S.—Received October 12, 1931.)

Introduction.

Since the publication of Christiansen and Kramer's theory of chain reactions* numerous researches have now established the main criteria† by means of which such reactions may be recognised. These distinctive criteria describe, in a general manner, how the chains are propagated and terminated. In recent work on chain reactions in the gas phase, however, attention has to a large extent been directed to elucidating the mechanism of the initiation of the chains. This work has revealed a rather strange type of chemical reaction which is partly heterogeneous and partly homogeneous. The interpretation of the experiments, at present, suggests that the reaction is initiated at a surface, is then propagated through the gas phase and finally ends either in the gas phase or at a surface.

* 'Z. Phys. Chem.,' vol. 104, p. 451 (1923).

† Hinshelwood, "Ann. Rep. Chem. Soc.," p. 41 (1930).

For example, it has now been shown* that a mixture of hydrogen and oxygen which normally explodes in a hot quartz or porcelain vessel does not ignite when brought into a large vessel under conditions in which the hydrogen and oxygen do not have an opportunity of diffusing to the walls of the containing vessel. If a hot quartz or iron rod at the same temperature is introduced into the gas mixture explosion occurs. Similarly, a hot mixture of carbon disulphide vapour and oxygen may be ignited by introducing a glass rod at the same temperature into the gases.† A third example of the initiation of reaction chains at a surface is given by the non-explosive oxidation of propane.‡

These experiments suggested that conditions might be found for the chain oxidation of phosphorus vapour in which the reaction is initiated at an interface in the reaction vessel. Since the kinetics of the chain propagation have been worked out in some detail by Semenoff and co-workers,§ a study of the kinetics of the reaction would show whether suitable conditions have been realised. Further, since chain oxidations resemble each other in many respects, it was also desirable to find conditions for the oxidation of phosphorus vapour occurring completely at a surface. The phenomena of the oxidation of phosphorus would then resemble the oxidation of hydrogen which may occur at an interface, or as a chain reaction, the chains being stable or unstable according to the conditions of the experiment.

The action of hot metallic filaments on mixtures of phosphorus vapour and oxygen at pressures below the lower explosion limit was therefore investigated in detail. The metals used were platinum, gold, silver, tungsten and molybdenum. Some preliminary experiments had been carried out by Chariton and Walta,|| but the course of the reaction was followed by a method, which, as Bodenstein¶ pointed out, gave misleading results. These results will be considered later.

The experiments recorded below point to the conclusion that, in presence of platinum the reaction takes place entirely on the surface of the filament.

* Alyea and Haber, 'Z. Phys. Chem.,' vol. 10, B, p. 193 (1930); Alyea, 'J. Amer. Chem. Soc.,' vol. 53, p. 1324 (1931); compare also Garstang and Hinshelwood, 'Proc. Roy. Soc.,' A, vol. 130, p. 640 (1931); and H. S. Taylor, 'Chem. Rev.,' vol. 9, p. 12 (1931).

† H. W. Thompson, 'Naturwiss,' vol. 22, p. 530 (1930); 'Z. Phys. Chem.,' vol. 10, B, p. 273 (1930).

‡ Pease, 'J. Amer. Chem. Soc.,' vol. 51, p. 1829 (1929).

§ 'Z. Physik,' vol. 46, p. 109 (1927); 'Z. Phys. Chem.,' vol. 4, B, p. 288 (1929).

|| 'Z. Physik,' vol. 39, p. 547 (1926).

¶ 'Z. Physik,' vol. 41, p. 548 (1927).

Tungsten, on the other hand, is able to initiate the reaction at its surface, the chains then spreading into the gas and presumably terminating on the walls of the reaction tube. Gold and silver exhibited similar behaviour to that of tungsten, but the reaction was only measurable when the temperature of the filament was close to the melting point of these metals. Frequent fusion of the filaments occurred so that an extended investigation of the reaction could not be carried out.

Experimental Method and Apparatus.

The experimental method used throughout was somewhat unusual and will therefore be described in detail. The difficulty which had to be overcome was to measure pressures of oxygen of 10^{-2} mm. of mercury in presence of phosphorus (and in some cases in presence of foreign gases) with an accuracy of about 2 per cent. It is not possible to use a McLeod gauge preceded by liquid air trap to follow the changing pressure of oxygen (*cf.* Bodenstein, *loc. cit.*). Glass spring manometers and sulphuric acid manometers are not sensitive enough. The quartz fibre manometer cannot be used to measure the rate of a reaction which takes place to 50 per cent. of its full extent in 5 minutes, while the Pirani-Hale gauge requires recalibration for changing environment of the filament, *e.g.*, diameter of reaction tube, presence of inert gases and changing phosphorus concentration.

The method finally adopted made use of the known value of the critical oxidation pressure. In short, the method consisted in adding a known amount of oxygen to the phosphorus vapour, heating up the filament for the desired time and then determining how much oxygen had to be added to bring its pressure up to the critical value.

The arrangement of the apparatus is shown in fig. 1. R is the reaction tube (diameter 2 cm.) connected at the top to reservoirs of phosphorus vapour, inert gas and through the capillary C to the oxygen reservoir. The filament is supported by degassed nickel wire which in turn is connected to borated copper wire passing through the pinch seal. The reaction tube is divided by the ground joint G which permits of "liners" of glass tubing* being put into position inside R thereby decreasing its effective diameter. In this way the same filament could be used conveniently and rapidly in reaction tubes of different diameter. The pumping system consisted of a liquid air trap followed by a three-stage mercury condensation pump which was backed by a "Hyvac"

* The volume of glass in the "liner" was less than 1 per cent. of the volume of the reaction tube and connections.

oil pump. The filament, about 15 cm. long, was situated near the axis of R. In order to keep its temperature constant the filament formed part of a Wheatstone bridge, the current for the bridge being supplied through a potentiometer from a battery of accumulators.

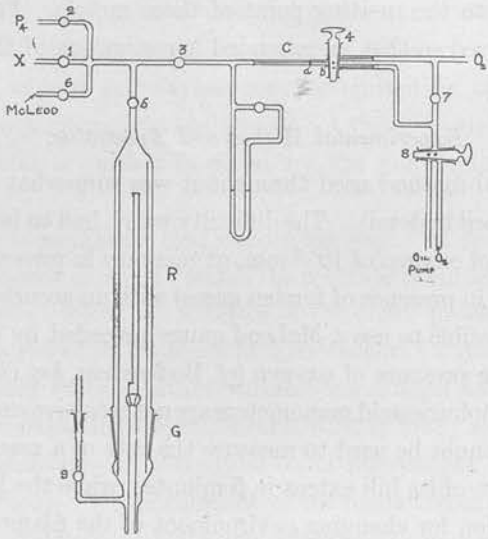

FIG. 1.

With taps 1, 6 and 9 closed and 2, 3 and 5 open, 4 was turned so that C was connected to the oxygen reservoir; simultaneously the stop-watch was started and the time for explosion determined (T_1). R was then pumped out and filled with phosphorus vapour. When oxygen had been allowed to flow into R for the requisite time (T_2), the barrel of 4 was rotated quickly through 180°, 8 being open to the pump. The pressure of oxygen in a–b was therefore reduced suddenly to a small fraction of its former value and hence the flow through C practically instantaneously arrested. The volume of tube a–b was about 0·05 c.c. while the oxygen reservoir held 1 litre. Separate control experiments showed that no appreciable error arose in this method of admitting the oxygen to the reaction tube. The filament was then heated up for the desired time, after which the flow of oxygen was started and the time (T_3) required for the oxygen pressure to rise to the critical value was noted. The amount of oxygen used up in the reaction is $T_2 + T_3 - T_1$, and the fraction of oxygen used is $(T_2 + T_3 - T_1)/T_2$.

In some of the best experiments when the critical oxidation pressure remained steady the time of explosion could be repeated to within 1/5 second with an explosion time of 60 seconds. This very desirable constancy was not pre-

served for long, the critical pressure usually drifting slightly throughout a series of experiments. Corrections (not given in the tables) were applied whenever this drift occurred.

The source of phosphorus vapour was white phosphorus obtained by heating anhydrous red phosphorus *in vacuo*. The oxygen used was obtained from a cylinder. (No difference in results was observed if pure electrolytic oxygen was used instead of cylinder oxygen.) The argon contained 1 per cent. nitrogen and the neon 2 per cent. helium.

Platinum Filament.

The first wires used had a diameter of 0·1 mm., but after a few experiments they became brittle and fell to pieces. Somewhat thicker wires (0·3 mm.) were substituted; these lasted very much longer, although after a large number of experiments they, too, fell to pieces. The reaction velocity was conveniently measurable when the temperature of the wire was below red heat, and when the activity of the wire became steady the temperature used was about 200° C. A new wire had always a much greater activity than one which had been used for several experiments. The activity of an old wire could be increased greatly by heating it to redness *in vacuo* for a few minutes. This treatment shortened the life of a wire considerably. Throughout its life the catalytic activity of the wire varied somewhat irregularly. This rendered accurate comparison of long series of results impossible. It was therefore almost impossible to make reliable measurements of the temperature coefficient of the reaction.

Table I gives the results of two typical series of experiments.

Table I.

Initial concentration of O_2 (sec.).	Amount of O_2 used up (sec.).	Fraction of O_2 remaining (O_2r).	$-\log_{10} O_2r$.	Time of heating of filament.
				mins.
55	8·8	0·84	0·076	1
55	16·9	0·69	0·161	2
55	20·7	0·62	0·208	3
55	25·7	0·53	0·276	4
55	30·9	0·44	0·357	5
55	33·7	0·39	0·409	6
55	36·0	0·35	0·456	7
35	15·2	0·57	0·244	1
35	19·3	0·45	0·347	2
35	23·6	0·33	0·481	3
35	26·5	0·24	0·620	4
35	29·4	0·16	0·696	5

The second series of results was obtained with the same wire as was used for the first series. At the end of the first series the wire was heated to redness *in vacuo* and as shown in fig. 2: an increase in activity results. Since the result of plotting $-\log_{10} O_2 r$ ($O_2 r$ = fraction of oxygen remaining) against the time of heating the wire is a straight line, the reaction must be unimolecular with respect to the oxygen molecule.

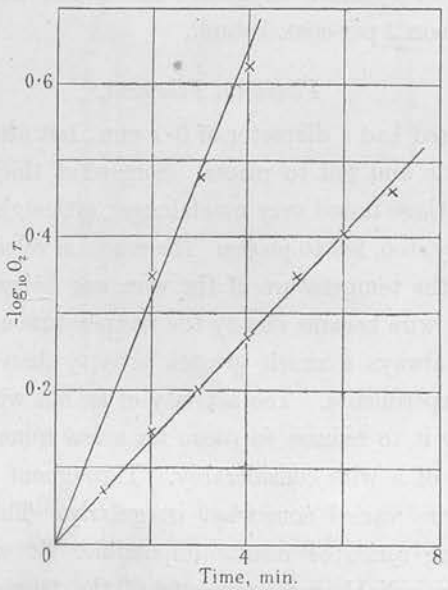

FIG. 2.—Plot of reaction time against the logarithm of the fraction of oxygen remaining showing that the reaction rate is proportional to $[O_2]$.

Table II gives four series of results using different concentrations of phosphorus vapour.

These results are shown graphically in fig. 3, where it is seen that although the pressure of phosphorus changes from 0·0014 mm. to 0·038 mm., a 27-fold increase, the reaction velocity varies irregularly between small limits. This variation may be ascribed to the varying activity of the wire. It is reasonable to assume, therefore, that the reaction velocity is independent of the concentration of the phosphorus vapour.

The influence of argon on the velocity of the reaction was next investigated. The pressure of argon was measured by the sulphuric acid manometer. The results are given in Table III. These results were obtained at different times in the life of the filament.

The argon is therefore without influence on the velocity of the reaction.

Table II.

Pressure of phosphorus (mm. Hg).	Initial concentration O_2 (sec.).	Amount of O_2 used up (sec.).	O_2r.	—log Or.	Time of heating. (mins.).
0·0014	45	15·4	0·66	0·180	1
	45	16·2	0·64	0·194	2
	45	19·6	0·56	0·252	3
	45	22·7	0·49	0·310	4
0·0043	50	9·2	0·82	0·086	1
	50	11·5	0·77	0·113	2
	50	14·2	0·72	0·143	3
	50	17·7	0·65	0·187	4
	50	21·0	0·58	0·237	5
	50	24·5	0·51	0·293	6
0·0043	50	7·4	0·86	0·065	1·2
	50	11·6	0·77	0·114	2
	50	15·2	0·70	0·155	3
	50	19·8	0·60	0·222	4
	50	23·1	0·54	0·268	5
	50	33·6	0·33	—	6
0·038	50	9·5	0·81	0·091	1
	50	14·2	0·72	0·143	2
	50	19·0	0·62	0·208	3
	50	23·6	0·53	0·276	4
	50	33·8	0·33	0·481	5
	50	44·6	0·11	—	6

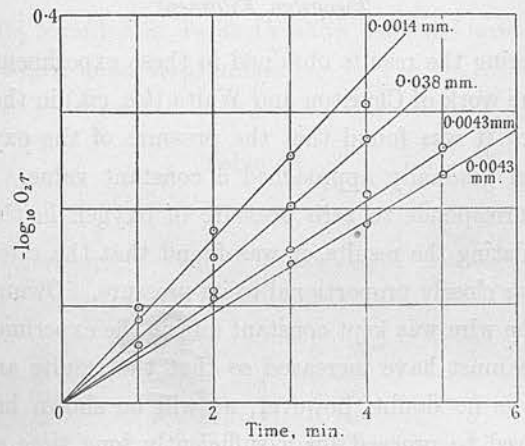

FIG. 3.—Irregular variation of reaction velocity within small limits with widely varying concentration of phosphorus.

Another observation of importance serves as a reliable guide to the nature of the reaction when it is considered in relation to the behaviour of tungsten. If oxygen is allowed to leak into the reaction vessel filled with phosphorus

Table III.

Initial concentration of O_2 (sec.).	Time of heating (mins.).	Pressure of argon (mm. Hg).	Amount of O_2 used (sec.).
30	2	0	30·0
30	2	0·054	32·6
30	4	0	14·8
30	4	0·081	12·2
30	4	0	17·4
30	4	0·081	15·0
30	4	0	21·1
30	4	0·081	22·6
30	2	0	13·6
30	2	0·135	12·6
30	2	0	13·0
30	2	0·135	11·2

vapour until a glow appears and then the current is switched on in the platinum wire the glow is immediately extinguished.

The two facts, (*a*) velocity of reaction independent of phosphorus and argon concentration, and (*b*) absence of glow during the reaction, would thus appear to point to the reaction occurring on the surface of the platinum wire. The low temperature at which the wire functions would also tend to uphold this point of view.

Tungsten Filament.

Before considering the results obtained in these experiments it is necessary to re-examine the work of Chariton and Walta (*loc. cit.*) in the light of Bodenstein's criticism. It was found that the pressure of the oxygen fell rapidly at first and then gradually approached a constant value. If this constant value actually corresponds to zero pressure of oxygen in the reaction tube, then, on recalculating the results, it was found that the rate of consumption of the oxygen was closely proportional to its pressure. Owing to the fact that the current in the wire was kept constant during the experiment, the temperature of the wire must have increased so that the results are not absolutely reliable. There is no doubt, however, as will be shown below, that if the reaction is allowed to proceed for a sufficiently long time all the oxygen is used up.

In the experiments with tungsten filaments it was first of all ascertained that the velocity of the reaction was conveniently measurable at temperatures where the oxidation of the tungsten wire itself was negligible. During these preliminary experiments it was found that the activity of the tungsten wire

did not deteriorate with use, but remained fairly constant throughout a large number of experiments. The diameter of the wire used was 0·1 mm.; it was mounted in nickel supporting leads. Another precaution which enabled more reproducible results to be obtained consisted in heating the wire for 2 minutes to the same temperature as that used for the experiments previous to the carrying out of each experiment. If this heating was omitted the critical oxidation pressure was always slightly low. This was probably due to the wire being covered with a layer of phosphorus pentoxide deposited thereon from the previous experiment. Since the wire formed an interface in the reaction tube and therefore was in a condition to stop reaction chains, it was quite conceivable that the nature of the surface presented to the chains might alter the efficiency of their termination. The removal of the layer of pentoxide increased the critical pressure by about 10 per cent., so that it would appear that phosphorus pentoxide is not so efficient in stopping the chains as a tungsten surface covered (in this case probably) by a layer of oxygen atoms.

Further, although a fairly efficient pumping system was used, the time of pumping out the reaction tube was kept the same for every experiment. In addition, all operations such as the heating up and cooling down of the filament, the preliminary heating of the filament, etc., were kept to a strict time schedule so that there would be as small a variation in results as was experimentally possible.

The experiments recorded in Table IV show that the order of the reaction with respect to oxygen molecule is unity.

Table IV.

Initial concentration of O_2 (sec.).	Amount of O_2 used up (sec.).	O_2r.	$-\log_{10} O_2r$.	Time of heating (mins.).	$-\log O_2r$ / Time of heating.
40	18·6	0·53	0·276	1	0·276
40	23·8	0·40	0·398	2	0·199
40	27·4	0·31	0·509	3	0·169
40	32·9	0·18	0·745	4	0·186
40	34·8	0·13	0·886	5	0·177
40	37·1	0·07	1·155	6	0·192
55	19·7	0·64	0·194	1	0·194
55	28·9	0·48	0·319	2	0·159
55	35·6	0·35	0·456	3	0·152
55	41·6	0·24	0·620	4	0·154
55	46·3	0·16	0·796	5	0·159
55	49·6	0·10	1·000	6	0·166

Table V gives five series of results with varying concentrations of phosphorus vapour. The temperature of the wire was maintained constant and the experiments were carried out in the order given below.

Table V.

Pressure of phosphorus (mm.).	Initial concentration of O_2 (sec.).	Amount of O_2 used up (sec.).	O_2r.	Time of heating.	$-\log O_2r$.
0·007	40	1·0	0·975	2	0·011
		2·0	0·950	3	0·022
		4·8	0·880	4	0·055
		8·4	0·790	5	0·102
0·026	40	9·4	0·77	1	0·116
		12·4	0·69	1	0·161
		13·4	0·66	2	0·180
		16·4	0·59	3	0·229
		20·0	0·50	4	0·301
0·026	40	9·8	0·76	1	0·119
		11·0	0·72	2	0·143
		14·6	0·64	3	0·194
		18·4	0·54	4	0·268
		22·6	0·43	5	0·367
0·007	50	2·4	0·952	1	0·022
		4·0	0·920	2	0·036
		6·0	0·880	3	0·055
		7·4	0·852	4	0·079
		8·0	0·840	5	0·081
0·017	50	5·0	0·900	2	0·046
		3·5	0·892	2	0·050
		8·2	0·836	3	0·078
		11·8	0·764	4	0·117
		15·4	0·692	5	0·160
Velocity constant....	0·07	0·08	0·13	0·34	
Pressure of P	0·007	0·007	0·017	0·026	

From these results the rate of the reaction is very nearly proportional to the first power of the concentration of the phosphorus vapour.

Temperature Coefficient of the Reaction.—To make the investigation of this reaction complete the temperature coefficient was measured in order to calculate the apparent heat of activation. The temperature of the wire was obtained from its resistance which could be immediately read off from the bridge. No corrections were applied for the cooling effect of leads. The resistance/temperature equation used was that experimentally established by Langmuir.*

The method of carrying out the experiments was somewhat modified, so that rapid comparison of velocity constants could be made with the filament at different temperatures. The time of heating of the filament was kept constant throughout a series and the velocity constant for each experiment was calcu-

* "International Critical Tables," vol. 6, p. 136.

lated by the usual logarithmic formula. The pressure of phosphorus vapour was maintained constant at 0·007 mm. during all temperature coefficient measurements. Table VI (fig. 4) shows in detail the record of a series of experiments, while Table VII summarises the data from other experiments. The heat of activation is thus comparatively small. Its significance will not be discussed until other factors influencing the reaction have been investigated.

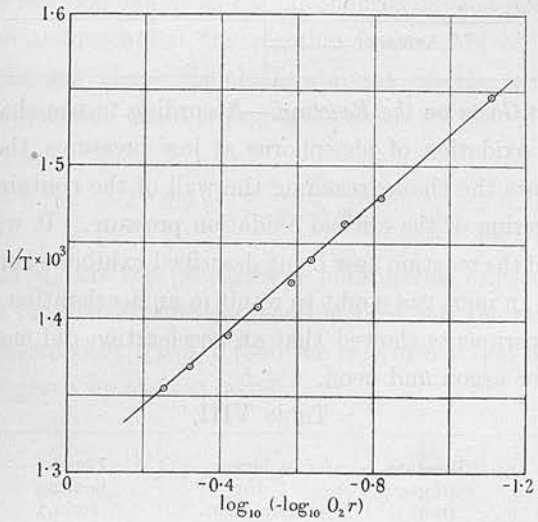

FIG. 4.—Temperature coefficient of reaction. — $\log_{10} O_2 r$ is equal to the velocity constant since time of the reaction was maintained constant.

Table VI.

Temperature of wire °K.	Initial concentration of O_2 (sec.).	Time for explosion (sec.).	Time of heating (min.).	Amount of O_2 used up (sec.).	$O_2 r$.	$-\log O_2 r$.
666	0	45·4	0			
666	40	19·0	2	13·6	0·70	0·155
675	0	47·8	0			
675	40	21·2	2	13·4	0·70	0·155
684	0	48·6	0			
684	40	24·4	2	15·8	0·65	0·187
693	0	49·6	0			
693	40	28·0	2	18·4	0·59	0·229
702	0	50·8	0			
702	40	31·2	2	20·4	0·55	0·260
711	0	52·0	0			
711	40	35·4	2	23·4	0·48	0·319
720	0	54·0	0			
720	40	40·6	2	26·6	0·41	0·387
728	0	55·0	0			
728	40	45·0	2	30·0	0·33	0·481
737	0	56·8	0			
737	40	49·6	2	32·8	0·27	0·569

Table VII.

Series number.	Heat of activation.
	k. cal.
W.34	14
W.37A	16
W.37B	18
W.38	14
W.39	17
Average	16

Effect of Inert Gases on the Reaction.—According to the chain theory of the kinetics of the oxidation of phosphorus at low pressures, the presence of an inert gas prevents the chains reaching the wall of the containing vessel; this results in a lowering of the critical oxidation pressure. It would be expected therefore that, if the reaction now being described exhibits chain characteristics, the presence of an inert gas ought to result in an acceleration of the oxidation. Preliminary experiments showed that an acceleration did ensue. Table VIII shows results for argon and neon.

Table VIII.

Initial concentration of O_2 (sec.).	Pressure of gas (mm.).	Time for explosion.	Time of heating (min.).	Amount of O_2 used up (sec.).
		Argon.		
0	—	40·4	—	—
0	0·089	27·6	—	—
25·0	—	31·6	2	16·2
25·0	0·089	31·4	2	28·8
0	—	47·8	—	—
0	0·135	27·4	—	—
25·0	—	38·0	2	15·2
25·0	0·135	35·0	2	22·6
0	—	49·6	—	—
0	0·087	33·6	—	—
25·0	—	39·4	2	14·8
25·0	0·087	36·2	2	27·6
		Neon.		
0	—	55·4	—	—
30	—	31·8	1	6·4
0	0·103	43·6	—	—
30	0·103	24·4	1	9·8
0	—	61·8	—	—
30	—	38·4	1	6·6
0	0·130	44·6	—	—
30	0·130	26·4	1	11·8
0	—	61·6	—	—
30	—	39·6	1	8·0
0	0·162	42·4	—	—
30	0·162	25·4	1	13·0

The effect of neon is not quite so great as that for argon. This is to be expected, since owing to its smaller mass and diameter the neon atom is not so effective in preventing the reaction chains from reaching the walls of the reaction tube.*

The quantitative calculation of the effect of inert gases is somewhat complicated and the following treatment is based on Semenoff's† expression for the length of the reaction chains in the phosphorus oxygen reaction.

It will now be assumed that the reaction in presence of hot tungsten is propagated in the gas phase, the chains starting on the tungsten filament. The length of the reaction chain is proportional to

$$p_P \cdot p_O \left(1 + \frac{p_X}{p_P + p_O}\right) d^2,$$

where p_P, p_O and p_X are the pressures of phosphorus, oxygen and inert gas respectively, d is the diameter of the reaction tube. If the rate of starting of the chains is represented by $f(p_O p_P)$, then the rate of reaction which is equal to $-dp_O/dt$ will be given by the expression

$$-\frac{dp_O}{dt} = Kf(p_O p_P)\, p_O p_P \left(1 + \frac{p_X}{p_P + p_O}\right) d^2. \qquad (1)$$

where K is a constant. Since it has been shown that the rate of the reaction is proportional to $p_P \cdot p_O$ the value of $f(p_O \cdot p_P)$ must be independent of the concentration of P_4 and O_2, so that (1) simplifies to

$$-\frac{dp_O}{dt} = Kp_O \left(1 + \frac{p_X}{p_P + p_O}\right), \qquad (2)$$

K being another constant. p_P and d are for the present being maintained at constant values. Rearranging (2) and integrating

$$-Kt = \int \frac{dp_O}{p_O\left(1 + \frac{p_X}{p_P + p_O}\right)}, \qquad (3)$$

or

$$-Kt = \tfrac{1}{2} ln\, p_O (p_O + p_P + p_X) + \left\{p_P - \frac{p_P + p_X}{2}\right\} \frac{1}{p_P + p_X} ln \frac{p_O}{p_O + p_P + p_X} + \text{const.}$$

* 'Proc. Roy. Soc.,' A, vol. 132, p. 108 (1931).

† 'Z. Phys. Chem.,' vol. 2B, p. 161 (1929).

Therefore

$$-\mathrm{K}t = \frac{p_\mathrm{P}}{p_\mathrm{P}+p_\mathrm{X}}\, ln\, p_\mathrm{O} + \frac{p_\mathrm{X}}{p_\mathrm{P}+p_\mathrm{X}} \cdot ln\,(p_\mathrm{O}+p_\mathrm{P}+p_\mathrm{X}) + \text{const.} \quad (4')$$

(If $p_\mathrm{X} = 0$ this expression $= ln\, p_\mathrm{O} + \text{const.}$, as would be expected.)

Now since p_X is much greater than p_P, *e.g.*, in most experiments $p_\mathrm{X} > 0{\cdot}1$ mm. and $p_\mathrm{P} = 0{\cdot}007$ mm. (4') may be simplified to

$$-\mathrm{K}t = \frac{p_\mathrm{P}}{p_\mathrm{X}}\, ln\, p_\mathrm{O} + ln\,(p_\mathrm{O}+p_\mathrm{X}) + \text{const.} \quad (5)$$

There is a further complication to be disposed of. p_X must be multiplied by the appropriate diffusion coefficient. It has been shown* that for mesitylene the equation

$$p_\mathrm{O}\, p_\mathrm{P}\left(1 + \frac{p_\mathrm{X}}{p_\mathrm{P}+p_\mathrm{O}}\right) = \text{const.} \quad (6)$$

holds since the value of the constant obtained when $p_\mathrm{X} = 0$ is equal to that obtained when an experimentally observed value of p_O for a given p_X is inserted in the equation. To allow for gases which do not lower the explosion limit to the same extent as mesitylene (6) is written in the form

$$p_\mathrm{O} p_\mathrm{P}\left(1 + \frac{\mathrm{A_X/A_M} \cdot p_\mathrm{X}}{p_\mathrm{P}+p_\mathrm{O}}\right) = \text{const.} \quad (7)$$

A is the slope of the line obtained by plotting $1/p_\mathrm{O}$ against $(1 + p_\mathrm{X}/p_\mathrm{P} + p_\mathrm{O})$ and $\mathrm{A_X}$ and $\mathrm{A_M}$ are the values of A for the gas used in the experiment and for mesitylene respectively. Introducing this correction into (5) and evaluating the constant of integration, the velocity constant K is given by

$$\mathrm{K} = \frac{1}{t}\, ln\left\{\left(\frac{p'_\mathrm{O}}{p_\mathrm{O}}\right)^{p_\mathrm{P}/\mu p_\mathrm{X}} \cdot \frac{(p'_\mathrm{O}+\mu p_\mathrm{X})}{(p_\mathrm{O}+\mu p_\mathrm{X})}\right\}, \quad (8)$$

where p'_O and p_O are the initial and final pressures of oxygen for a reaction time t., $\mu = \mathrm{A_X/A_M}$.

Table IX gives two separate sets of results for neon. These are shown graphically in fig. 5, where it is seen that the velocity constant calculated from (8) is independent of p_X.

* 'Proc. Roy. Soc.,' A, vol. 132, p. 108 (1931).

Table IX.

Pressure of neon (mm.).	Initial concentration of O_2 (sec.).	Amount of O_2 used up (sec.).	O_2r.	$-\log O_2r$.	log Z.	Time of heating (mins.).
			Series A.			
0·216	28	11·4	0·59	—	0·177	0·5
	28	19·4	0·31	—	0·352	1·0
	28	23·3	0·17	—	0·481	1·5
0·000	28	9·7	0·65	0·185	—	0·5
	28	14·2	0·49	0·306	—	1·0
	28	20·4	0·27	0·568	—	1·5
	28	23·8	0·15	0·823	—	2·0
	28	27·0	0·03	1·531	—	2·5
			Series B.			
0·095	30	9·4	0·69	—	0·147	0·5
		16·0	0·47	—	0·284	1·0
		19·7	0·34	—	0·390	1·5
		22·4	0·25	—	0·478	2·0
		24·9	0·17	—	0·578	2·5
0·080	35	7·7	0·78	—	0·113	0·5
		14·0	0·60	—	0·260	1·0
		20·1	0·43	—	0·354	1·5
		23·8	0·32	—	0·457	2·0
		28·4	0·19	—	0·626	2·5
0·146	35	10·3	0·71	—	0·120	0·5
		17·2	0·51	—	0·233	1·0
		24·3	0·30	—	0·389	1·5
		27·9	0·20	—	0·485	2·0

$$Z = \left(\frac{p'_0}{p_0}\right)^{p_P/\mu p_X} \cdot \frac{p'_0 + \mu p_X}{p_0 + \mu p_X}.$$

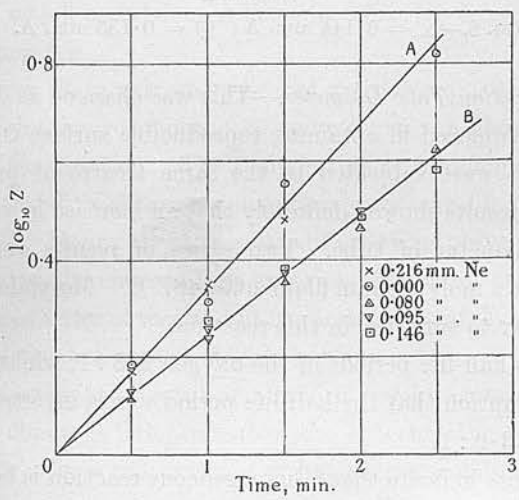

FIG. 5.—× = 0·216 mm. Ne; ⊙ = 0·000; △ = 0·080; ▽ = 0·095; ⊡ = 0·146.

Table X gives two sets of results for argon (fig. 6).

Table X.

Pressure of argon.	Initial concentration of O_2 (sec.).	Amount of O_2 used up (sec.).	O_2r.	log Z.	Time of heating (mins.).
0·144	30	8·5	0·72	0·065	0·5
		15·8	0·47	0·129	1·0
		21·5	0·28	0·193	1·5
		24·4	0·19	0·230	2·0
0·135	30	10·0	0·67	0·072	0·5
		15·6	0·48	0·125	1·0
		20·9	0·30	0·181	1·5
		24·6	0·18	0·231	2·0

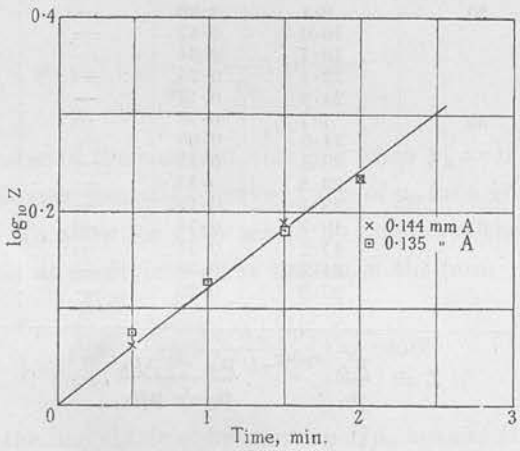

FIG. 6.—× = 0·144 mm. A; ⊡ = 0·135 mm. A.

Variation of Reaction Tube Diameter.—This was changed as described above. Difficulty was experienced in obtaining reproducible surface conditions even if the reaction tubes were subjected to the same treatment previous to their being used. The results showed definitely that an increase in velocity occurred with increased diameter of tube. Two series of results are given. These were obtained with a molybdenum filament at 487° C. Molybdenum functioned in a similar manner to tungsten in this reaction.

The ratio of the half-life periods of the oxygen is 3 : 1, whilst the theoretical value on the assumption that the half-life period varies inversely as the square of the diameter is 3·0 : 1.

These experiments indicate that a homogeneous reaction is being considered. Visible proof of this opinion is given by the fact that a glow is emitted during

Table XI.

Diameter of tube = 1·9 cm. Initial conc. of oxygen = 55 secs.				Diameter of tube = 1·1 cm. Initial conc. of oxygen = 30 secs.			
Amount of O_2 used up (sec.).	O_2r.	$-\log O_2r$.	Time of heating (mins.).	Amount of O_2 used up (sec.).	O_2r.	$-\log O_2r$.	Time of heating (mins.).
24·2	0·56	0·252	0·5	4·5	0·85	0·070	0·5
31·4	0·43	0·367	1·0	8·4	0·72	0·143	1·0
36·5	0·34	0·469	1·5	11·1	0·63	0·201	1·5
38·8	0·29	0·538	2·0	14·0	0·53	0·276	2·0
40·5	0·26	0·585	2·5	16·3	0·46	0·336	2·5

the progress of the reaction. The glow is entirely similar, so far as the eye can discern, to the glow obtained in the explosive reaction between phosphorus and oxygen. Its intensity is directly dependent on the speed with which the reaction goes forward. It does not persist when the current in the filament is switched off, but it reappears gradually when the current is switched on again. This process can be repeated until the glow becomes too faint to be seen. It is of interest to note here that in the slow oxidation of phosphorus at pressures above the upper explosion limit no glow can be detected even with sensitive detectors.*

As was stated, molybdenum filaments behave similarly to tungsten with respect to their action on phosphorus/oxygen mixtures. Moreover, the temperature at which molybdenum becomes effective is nearly equal to that observed for tungsten.

Gold and silver filaments when heated to the requisite temperature also induce the combination of phosphorus and oxygen. A glow is emitted during the progress of the reaction. The temperature to which gold and silver have to be raised in order to obtain a conveniently measurable reaction velocity is close to 1000° C. Hence there is great difficulty in preventing the filaments from fusing during the course of an experiment. Many attempts were made to obtain extended series of results, but the destruction of several of the filaments prevented this being accomplished.

From the experiments described above it would appear that the rate of starting of the chains is independent of the concentrations of the phosphorus and the oxygen. Since the presence of hot tungsten induces oxidation, some

* Rayleigh, 'Proc. Roy. Soc.,' A, vol. 106, p. 1 (1928).

material body must leave the tungsten surface, subsequently collide with and activate either a phosphorus or an oxygen molecule. This activated molecule then initiates the chain. Before suggesting how this process might occur there is one small point which may suggest a different mechanism for the starting of the reaction chain.

Although theory indicates that the length of the chain is proportional to concentration of phosphorus molecules, Semenoff* found experimentally that the chain length was proportional to the square root of the phosphorus concentration. This has been repeatedly confirmed during this and other work on this reaction. It may therefore be possible that the rate of starting of the chains is proportional to the square root of the phosphorus concentration so that the apparently simple experimental result covers a more complex mechanism.

Under the experimental conditions employed the tungsten surface was probably covered with a layer of oxygen atoms, but owing to the comparatively low temperature (450° C.), no oxygen-activated molecules or atoms or WO_3 would evaporate from the surface. Initiation of the chains owing to the evaporation of activated oxygen thus seems to be precluded. On the other hand, a phosphorus molecule might strike this layer of adsorbed oxygen and rebound taking an oxygen atom or molecule with it. This oxide might then start the reaction. This mechanism leads to the appearance of p_P^2 in the kinetics of the reaction and is therefore excluded.

A third possibility is that phosphorus itself is adsorbed as a completed unimolecular layer on the layer of oxygen atoms attached to the tungsten surface in the same way as cæsium, for example, is tenaciously held to a layer of oxygen on a silver surface. The evaporation of a phosphorus oxide molecule from this layer might initiate the reaction but, if the layer of phosphorus is saturated, the rate of evaporation of the oxide would be independent of the concentration of phosphorus molecules in the gas phase. Therefore, the rate of reaction would be proportional to p_P.

With these suggested explanations in view, further experiments are being carried out on this reaction.

We wish to express our thanks to Professor Kendall for continued encouragement, to the Carnegie Trustees and to the Trustees of the Moray Research Fund of Edinburgh University.

* 'Z. Physik,' vol. 46, p. 109 (1927).

Summary.

The action of hot filaments of platinum and tungsten on mixtures of phosphorus vapour and oxygen at pressures smaller than the lower explosion limit has been investigated in some detail.

With platinum it was found that the reaction rate is conveniently measurable with the filament at a temperature of about 200° C. The reaction velocity is directly proportional to the oxygen pressure. Argon is without influence on the rate of the reaction. No glow is emitted during the oxidation. The reaction therefore probably occurs at the platinum surface.

With the tungsten filament at 500° C. the rate of the reaction can be conveniently measured. This rate is proportional to the pressure of the oxygen and of the phosphorus. It is increased by using wider reaction tubes and by the presence of neon and of argon. A green glow accompanies the progress of the reaction. The apparent heat of activation is 16 k. cal. These facts are summarised in the equation

$$-\frac{dp_O}{dt} = kp_P p_O \left(1 + \frac{\mu p_X}{p_P + p_O}\right) d^2 \cdot e^{-U/RT},$$

where p_P, p_O and p_X are the pressures of phosphorus, oxygen and inert gas, k is constant, $\mu = 0{\cdot}46$ for argon and $0{\cdot}20$ for neon, d is the diameter of a cylindrical reaction tube, $U = 16$ k. cal.

The reaction thus probably starts on the tungsten surface, is propagated through the gas phase and finally ends on the wall of the reaction tube.

Gold, silver and molybdenum behave similarly to tungsten, but have not been studied in detail.

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PHOTOCHEMICAL DECOMPOSITION OF PHOSPHINE

IT is rather surprising to find that, although the photochemistry of ammonia has attracted considerable attention since Warburg's[1] work, no corresponding experiments have been carried out with the equally simple molecule of phosphine. Such experiments have now been in progress in this laboratory for some time.

The absorption spectrum of phosphine consists of a region of continuous absorption beginning at about 220 $\mu\mu$ and continuing to 185 $\mu\mu$, the limit of the spectrograph used. Preceding this continuous band there are three diffuse bands in the region 220-230 $\mu\mu$. No fine structure is exhibited by these bands. The spectrum, like that of ammonia, would appear to be of the predissociation type.

Light from zinc or aluminium sparks readily decomposes the phosphine into hydrogen and phosphorus, which is deposited as the red variety on the walls of the insolation tube. The experiments on the direct photochemical decomposition have not yet been completed. The mercury photosensitised reaction has, however, been investigated in some detail. The rate of decomposition is about ten times that of ammonia under the same conditions. It is dependent on the diameter of the reaction tube; for, as the diameter is decreased—that is, the surface volume ratio increased—there is a decrease in the rate of decomposition. For example, in tubes of 2 cm., 1 cm., and 0·5 cm. diameter, the rates are in the ratio 2·5 : 1·5 : 1. This would indicate that recombination of the products of dissociation occurs at the walls of the reaction tube. Argon has no effect on the velocity. On the other hand, oxygen increases the rate of decomposition as much as five times ($p_{PH_3} = 0{\cdot}05$ mm.; $p_{O_2} = 0{\cdot}05$ mm)., while the subsequent addition of argon (0·1 mm.) still further increases this rate. These observations are most plausibly explained if it is assumed that oxygen attacks the products of dissociation, thus preventing their recombination. The resulting oxide molecules then initiate a stable chain reaction between the undecomposed phosphine and the oxygen.[2]

These results partly explain an interesting observation of Hinshelwood and Clusius,[3] who found that on illuminating a $PH_3 - O_2$ mixture below the lower critical explosion pressure, the pressure to which the mixture had to be compressed in order to obtain explosion was lower than that of the unilluminated gases. A mercury lamp with a chlorine-bromine filter transmitting 250-280 $\mu\mu$ was used in these experiments. The effect was shown to have its origin in the phosphine molecule, but in view of the fact that phosphine itself does not absorb in the region 250-280 $\mu\mu$, it would seem that the incidental presence of mercury vapour resulted in the phosphine being decomposed by excited mercury atoms into hydrogen atoms and probably PH or PH_2 radicals, which produce the Hinshelwood-Clusius effect. Hinshelwood and Clusius concluded that the active material was present in the gas phase, but on repeating their experiment by exposing the mixture in one tube and determining the explosion pressure immediately after in another similar tube, the effect was not observed. That is, the effect is most probably a wall phenomenon, the illumination of the mixture producing a molecule or radical which is afterwards adsorbed on the walls; the latter are thereby enabled to reflect the chains more efficiently, thus decreasing the explosion pressure. It has also been found that pretreatment of the walls with atomic hydrogen results in a decreased explosion pressure.

H. W. MELVILLE.

Chemistry Department,
The University, Edinburgh, Feb. 25.

[1] *Sitzungsber. Preuss. Akad.*, p. 746; 1911.
[2] *Cf.* Dalton and Hinshelwood, *Proc. Roy. Soc.*, A, **125**, 294; 1929.
[3] *Proc. Roy. Soc.*, A, **129**, 589; 1930.

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THE OXIDATION OF PHOSPHORUS VAPOUR AT LOW PRESSURES.

By H. W. Melville.

Received 18th January, 1932.

Within the past few years a number [1] of chemical reactions have been studied which possess a rather peculiar characteristic. The addition of an inert gas to the reaction mixture results in an increase in the reaction velocity. Reactions which exhibit this behaviour are chain reactions. According to the theory of chain reactions this increase is explained by supposing that the chains are terminated when they encounter the wall of the reaction vessel. The presence of an inert gas, by decreasing the mean free path of the molecules in the reaction mixture prevents the chains from reaching the walls and thus enables the chain to be longer than it normally would have been; this results in an increase of the reaction velocity.

In chain reactions which proceed explosively, for example, the oxidation of phosphorus [2] and phosphine [3] at low pressures, the effect of inert gases is to accelerate the reaction velocity but the effect is made evident by the inert gas lowering the *lower* critical oxidation pressure. That is, the inert gas facilitates the occurrence of explosion.

The effect of the inert gas can be expressed quantitatively by an equation originally deduced by Semenoff.[2] If p_{P_4}, p_{O_2}, p_x, are the pressures of phosphorus, oxygen and inert gas respectively then, at the lower explosion limit,

$$p_{P_4} \cdot p_{O_2}\left(1 + \frac{p_x}{p_{P_4} + p_{O_2}}\right) = \text{constant} \quad . \quad . \quad . \quad (1)$$

[1] For example the H_2-O_2 reaction, Gibson and Hinshelwood, *Proc Roy. Soc.*, 119A, 591, 1928.

[2] Semenoff, *Z. Physik*, **46**, 109, 1927; *Z. physikal. Chem.*, **2B**, 161, 1929.

[3] Dalton and Hinshelwood, *Proc. Roy. Soc.*, **125A**, 295, 1929.

provided the explosions are confined to a vessel of a given size. N (1) indicates that the inert gas effect should be independent of the nat of the gas. This result is due to the assumption that the molecules O_2 and X have the same mass and diameter and that therefore the m free path is inversely proportional to the total pressure.

Subsequent work [4] on this effect has shown that (1) does not scribe exactly the effect of gases on the lower critical oxidation limit phosphorus. From (1) it is seen that if $1/p_{O_2}$ is plotted aga $1 + \dfrac{p_x}{p_{P_4} + p_{O_2}}$ a straight line should be obtained. The slope A this line is, however, dependent on the nature of X. It was found t when the diffusion coefficient D of oxygen molecule through X is mu plied by A an approximately constant quantity was obtained.

Recently H. W. Thompson [5] has found that a similar relation holds for the lower critical oxidation limit of hydrogen. The effect a extends to the oxidation of methane. Equation (1) is thus modifi (empirically) to

$$p_{P_4} \cdot p_{O_2}\left(1 + \frac{D^{-1}p_x}{p_{P_4} + p_{O_2}}\right) = \text{constant}^{*}. \quad . \quad .$$

In order to deduce this equation the original theory must be modifi to some extent. The problem is very complicated since the rate diffusion of a reaction chain involves the diffusion of the two propaga into a ternary mixture. Semenoff [6] has attempted an exact solution the case for the hydrogen-oxygen reaction assuming the propaga were H and excited HO_2 molecules. This treatment is not suitable the above case. Another attempt at an exact kinetic theory analy of the diffusion of reaction chains was made recently by Bursian a Sorokin,[7] but their treatment is not applicable in the present case sin these investigators assumed at the outset that the masses and diamet of the reacting molecules were equal.

The following consideration represents an attempt to obtain on as simple a basis as possible. Following Dalton and Hinshelwoo let the chain propagators be X_O and X_P and assume that X_O is produc spontaneously at a rate $k_1F(c)$ in the reaction mixture, that X_O collid with P_4 to give X_P and that X_P collides with O_2 to give X_O then for t stationary state.

$$\frac{dp_{X_O}}{dt} = k_1F(c) + \alpha k_2 p_{X_P} p_{O_2} - k_3 p_{X_O} p_{P_4} - K p_{X_O} = 0, \quad .$$

$$\frac{dp_{X_P}}{dt} = k_3 p_{X_O} p_{P_4} - k_2 p_{X_P} p_{O_2} - K p_{X_P} = 0 \quad . \quad . \quad .$$

α introduces the branching chain hypothesis. K is the rate at whi X_O and X_P reach the wall of the vessel and are destroyed. For t condition of explosion, *i.e.*, $p_{X_O} = \infty$

$$(\alpha - 1)k_3 p_{P_4} p_{O_2} = K(p_{O_2} + p_{P_4}) \quad . \quad . \quad .$$

[4] Melville and Ludlam, *Proc. Roy. Soc.*, **132A**, 108, 1931.
[5] See page 299.
* A misprint occurs in ref. 4 on p. 125. The letter D should be written D^{-1}
[6] *Z. physikal. Chem.*, **2B**, 169, 1929. [7] *Ibid.*, **12B**, 247, 1931.

According to the Einstein-Smoluchowski diffusion law the time (t) required for a molecule to reach a point distant x from the original position is connected with the diffusion coefficient of the molecule through the gas by the equation

$$x^2 = 2Dt \quad . \quad . \quad . \quad . \quad . \quad (6)$$

K is inversely proportional to t and D is inversely proportional to the total gas pressure (equal masses and diameters), and if x is the radius of a cylindrical reaction vessel then $K \sim \{x^2(p_{P_4} + p_{O_2} + p_x)\}^{-1}$ so that substituting in (5), (1) is obtained.

Consider now a single molecule diffusing through a ternary gas mixture in which the diffusion coefficients for each gas separately are D_1, D_2 and D_3. If t is the time required to diffuse a given distance then assume that

$$t \sim \frac{1}{D_1} + \frac{1}{D_2} + \frac{1}{D_3} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

For a single gas $D \sim \frac{1}{M^{\frac{1}{2}} p \sigma^2}$ where M is the molecular weight, p the the pressure, σ the molecular radius. Therefore

$$K \sim \frac{1}{1/D_1 + 1/D_2 + 1/D_3}$$
$$\sim (M_1^{\frac{1}{2}} p_1 \sigma_1^2 + M_2^{\frac{1}{2}} p_2 \sigma_2^2 + M_3^{\frac{1}{2}} p_3 \sigma_3^2)^{-1} \quad . \quad . \quad (8)$$

Let $\sigma_1 = \sigma_2$ and $M_1 = M_2$ these being constants of any particular reaction then multiplying (8) by $\sigma_1^2 M_1^{\frac{1}{2}}$

$$K \sim \left(p_1 + p_2 + \frac{\sigma_3^2 M_3^{\frac{1}{2}}}{\sigma_1^2 M_1^{\frac{1}{2}}} \cdot p_3\right)^{-1} \quad . \quad . \quad . \quad (9)$$

From (5) and (9)

$$p_{P_4} \cdot p_{O_2}\left(1 + \frac{\sigma_3^2 M_3^{\frac{1}{2}}}{\sigma_1^2 M_1^{\frac{1}{2}}} \cdot \frac{p_x}{p_{P_4} + p_{O_2}}\right) = \text{constant.} \quad . \quad (10)$$

The variable which determines the magnitude of the effect of X is thus $\sigma_3^2 M_3^{\frac{1}{2}}$. Let $\sigma_1^2 M_1^{\frac{1}{2}} = k$ and substituting for $\sigma_3^2 M_3^{\frac{1}{2}}$ the more complicated factor $\sigma_{AX}^2\left(\frac{1}{M_A} + \frac{1}{M_X}\right)^{-\frac{1}{2}}$ as demanded by the Stefan-Maxwell theory for the diffusion of a binary mixture (10) becomes

$$p_{P_4} \cdot p_{O_2}\left(1 + \frac{\sigma_{AX}^2 (1/M_A + 1/M_X)^{-\frac{1}{2}}}{k} \cdot \frac{p_x}{p_{P_4} + p_{O_2}}\right) = \text{constant} \quad (11)$$

where M_A and M_X are the molecular weights of the diffusing molecule and of X. σ_{AX} is the sum of the radii of A and X. M_A and σ_A will be mean values since they represent the effect of X_O and X_P.

It emerges, therefore, that the factor multiplying p_x is not the diffusion coefficient (it is only inversely proportional to it) but a factor expressing the molecular weight and effective collision diameter of the inert gas molecules. For some particular gas this factor will be equal to unity. In the phosphorus experiments it would appear that the more complicated organic molecules fulfil this condition. Thus (10) will assume the simpler form (1). For simpler molecules the factor is less than unity.

Inhibition in the Gas Phase.

If, in addition, the added gas X is able to stop the reaction chain the gas phase the equations developed above must be modified. T correction has been developed from a theory of Kowalski,[8] and it been shown [4] that

$$k'A = 1 - 1/a\, e^{-U/RT} \quad . \quad . \quad . \quad (1$$

where k' and a are constants and $e^{-U/RT}$ is the ratio of the numbe collisions stopping the chains to the total number of collisions of X the reaction chains. There is reason to believe [9] that a is not less t 0·1 and may possibly be equal to unity. In the latter case (12) may written

$$k'A = 1 - e^{-U/RT} \quad . \quad . \quad . \quad . \quad (1$$

and hence if $e^{-U/RT} = 1$, $A = 0$. If A has a value less than that e pected from the diffusion coefficient for X this deviation may be ascrib to the termination of reaction chains in the gas phase. This result a follows from equations (3) and (4) of Dalton and Hinshelwood, (3) be modified to

$$\frac{dp_{X_0}}{dt} = k_1F(c) + \alpha k_2 p_{X_P} p_{O_2} - k_3 p_{X_0} p_{P_4} - k_4 p_{X_0} p_X - K p_{X_0} = 0 \quad (1$$

the penultimate term representing the inhibitory effect of X. If $k_3 = k_2$, (5) becomes

$$(\alpha - 1) k_3 p_{P_4} p_{O_2} = K(p_{P_4} + p_{O_2} + p_X) \quad . \quad . \quad (1$$

or substituting the value of K

$$p_{P_4} \cdot p_{O_2} = \text{constant},$$

so that the lower critical oxidation limit is unaffected by the additi of X. The inhibitory effect thus balances the diffusion effect.

This inhibition may explain the relatively small influence of aceto and formaldehyde ethylal in Thompson's H_2/O_2 experiments. A wel defined inhibitory action has been found for the $P_4 - O_2$ reaction at lo pressures, tetraethyl lead being used.

If tetraethyl lead acts as an inert gas its effect should be approximate equal to that of mesitylene or methylene chloride, $A = 1{\cdot}30$ where from the results given in Table I., $A = 0{\cdot}74$. From equation (1 $e^{-U/RT} = 0{\cdot}4$, *i.e.* 1 collision in every 2·5 is effective in terminating th chain. For comparison the results for methylene chloride are given D for tetraethyl lead cannot be calculated since the molecular diamete has not yet been measured. An estimate of this magnitude may b made from the parachor and D finally calculated giving a value close t that for mesitylene.

Pressures are in mm. Hg. The two series of experiments were carrie out under slightly different conditions, which accounts for the smal difference in p_{O_2}, for $p_X = 0$.

Equation (13) also explains another peculiarity of the oxidation o phosphorus at low pressures. On Semenoff's theory atomic oxyge is one of the chain propagators. From the experiments of Harte

[8] *Z. physikal. Chem.*, **4B**, 288, 1929. [9] *Ibid.*, **2B**, 161, 1929.

and Kopsch [10] on the reactions of atomic oxygen with organic compounds (vapours) and other gases it would be expected that most organic compounds would act as inhibitors for the $P_4 - O_2$ reaction since these compounds are completely oxidised under the experimental conditions of Harteck and Kopsch. As is seen from (13), however, $e^{-U/RT}$ must be at least 0·1 or 1 in 10 collisions must be effective if inhibition is to be noted since the experimental error is of the order of 10 per cent. In the reaction tube employed by Harteck and Kopsch an oxygen atom could make as many as 10^5 collisions with other gas molecules present so that even if oxidation only occurred with a collision efficiency of 10^{-5} it would be readily detectable. The atomic oxygen technique is thus

TABLE I.

Methylene Chloride.				Tetraethyl Lead.			
p_X.	p_{O_2}.	$1/p_{O_2}$.	$\frac{p_X}{1+\frac{p_X}{p_{P_4}+p_{O_2}}}$.	p_X.	p_{O_2}.	$1/p_{O_2}$.	$\frac{p_X}{1+\frac{p_X}{p_{P_4}+p_{O_2}}}$.
0	0·068	14·7	1·00	0	0·054	18·5	1·00
0·027	0·055	18·2	1·45	0·032	0·041	24	1·67
0·054	0·041	24	1·82	0·035	0·041	24	1·73
0·070	0·032	31	2·2	0·054	0·036	28	2·25
0·081	0·034	29	2·4	0·059	0·035	29	2·40
0·089	0·026	38	2·7	0·068	0·029	35	2·90
0·097	0·029	34	2·8	0·076	0·033	31	2·93
0·119	0·019	53	3·7	0·078	0·026	38	3·36
0·135	0·017	59	4·2	0·084	0·026	38	3·50
0·162	0·014	71	5·2	0·095	0·023	43	4·16
0·170	0·013	77	5·5	0·108	0·022	46	4·80
0·197	0·011	91	6·5	0·122	0·019	53	5·70
0·216	0·009	110	7·4	0·122	0·018	56	5·98
0·219	0·008	120	7·6	0·138	0·013	80	8·1

much more sensitive than the low pressure explosions of $P_4 - O_2$ mixtures as a detector of oxidation by atomic oxygen. This explains the discrepancy between the two series of experiments.

At the upper critical explosion limit of phosphorus vapour termination of the chains takes place entirely in the gas phase. In the following treatment an attempt is made to calculate the efficiency of the deactivating process. It will be assumed (1) the influence of the size of the reaction tube is negligible; (2) X_0 is destroyed by collision with O_2 and (3) with X. Equations (3) and (4) are therefore written

$$\frac{dp_{X_0}}{dt} = k_1F(c) + \alpha k_2 p_{X_P} p_{O_2} - k_3 p_{X_0} p_{P_4} - k_4 p_{X_0} p_{O_2} - k_5 p_{X_0} p_X = 0 \quad (14)$$

$$\frac{dp_{X_P}}{dt} = k_3 p_{X_0} p_{P_4} - k_2 p_{X_P} p_{O_2} = 0 \quad . \quad . \quad . \quad (15)$$

Solving for p_{X_P}, then p_{X_0} and introducing the condition for explosion

$$k_3 p_{P_4}(\alpha - 1) = k_4 p_{O_2} + k_5 p_X \quad . \quad . \quad . \quad (16)$$

[10] *Z. Electrochem.*, **36**, 714, 1930; *Z. physikal. Chem.*, **12B**, 327, 1931.

p_{O_2} being the upper critical explosion pressure. There are ex... mental data in support of (15) from the experiments of a numb... authors. If $p_X = 0$, then $p_{O_2} \sim p_{P_4}$ which has been found to be ... case by Kowalski.[8] If p_{O_2} is kept constant p_X will increase with ... (Emeleus [11]). The presence of X reduces p_{O_2}—an effect which has ... known for many years. To enquire into this question more cl... (16) may be rearranged

$$p_{O_2} = \frac{k_3/k_5 p_{P_4} (\alpha - 1)}{k_4/k_5 + p_X/p_{O_2}} = \frac{k}{a' + px/p_{O_2}} \quad . \quad .$$

This equation has been found by Schacherl [12] to express the beha... of nitrogen peroxide with a considerable degree of accuracy. A num... of other substances also conform to this equation.[13] For a given ... stance k and a' are characteristic the reciprocals of k and of a' be... measure of the efficiency of X as a poison since they contain the con... k_5. The ratio k/a' according to (17) should be independent of X. T... relationships are shown in table II., the data being obtained from T... and Gorlacher's experiments.

TABLE II.

Gas.	a'.	K.	a'/K.	Efficiency ... Inhibitin... Collision...
Sulphur Dioxide . .	23	13520	390	6 × 10⁻...
Benzene	21	10800	510	8 × 10⁻...
Cyclohexane . . .	20	10100	500	9 × 10⁻...
Acetylene	11·3	7020	350	1·2 × 10⁻...
Methylcyclohexane . .	8·2	4530	550	1·8 × 10⁻...
Ethylene	1·75	1070	610	7 × 10⁻...
Propylene	0·35	168	480	5 × 10⁻...
Cyclohexene . . .	0·11	58	530	1·4 × 10⁻...
Isoprene	0·025	20	800	4 × 10⁻...
Iron Pentacarbonyl . .	0·0033	1·7	520	5 × 10⁻...

The common gases, *e.g.* N_2, CO_2, H_2, etc., have only a small effe... the upper critical limit and the results of different investigators are ... in very good agreement. If it is assumed that iron penta-carbon... as efficient a poison as tetraethyl lead then from the value of K the abs... values of the efficiency of the poison may be calculated. This is g... in the last column of the above table. It is of importance to note t... the efficiencies lie between 10^{-1} and 10^{-5} in agreement with the ... periments of Harteck and Kopsch.

Effect of Ozone and of Phosphine at Low Pressures.

The effect of ozone and of phosphine on the behaviour of P_4–... mixtures has also been investigated at low pressures, both gases gi... abnormal results. Kowalski had found [8] that ozone raises the u... critical explosion limit, that is, it facilitates the propagation of ... reaction chains. Corresponding to this, at low pressures ozone red...

[11] *J. Chem. Soc.*, 1336, 1926.
[12] *Coll. Czech. Chem. Comm.*, **2**, 665, 1930.
[13] Centnerszever, *Z. physikal. Chem.*, **26**, 9, 1898; Tausz and Gorlacher, *anorg. Chem.*, **190**, 95, 1930.

the critical explosion pressure. For instance, with less that 5 per cent. ozone in the oxygen the pressure of the mixture for explosion was about 20 per cent. less than that without ozone. It is evident therefore, that ozone decreases the explosion pressure in some way which is different from the normal diffusion effect since this would amount to a decrease of 1 to 2 per cent.

Phosphine has an exactly opposite effect—it *raises* the lower critical pressure of $P_4 - O_2$ mixtures. This effect is entirely unexpected from the theoretical point of view, for if PH_3 is a strong inhibitor *in the gas phase* it should have little or no influence. This seems to indicate that the effect is connected with the initiation of the chains. But theory shows that the explosion limit is not affected by the rate of production of the centres which start the chains providing, of course, that a finite number of centres is produced. It may be that phosphine can reduce this number to such a small value that the explosion limit is affected. While it has not yet been proved whether the chains in this particular

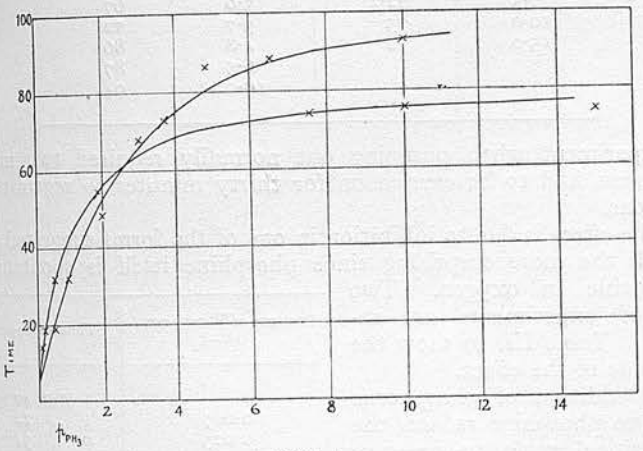

FIG. 1.

reaction are initiated in the gas phase or at an interface, it would appear that an interface is more suitable than the gas phase for inhibition to exert its full influence.

On the other hand if the chains can make elastic collisions with the walls of the containing vessel it is probable that the condition of the wall may alter the explosion pressure. Experiments have been made with walls of various substances, " clean " glass, paraffin wax, platinum, but no significant variations were obtained. This was probably due to the walls being covered with oxides of phosphorus since several explosions must take place in any one tube in order to measure the critical pressure. Owing to an accident during the course of these experiments one of the reaction tubes was covered with a layer of concentrated sulphuric acid from an adjacent manometer. It was then found that in this tube the explosion pressure had fallen to about half its initial value. That is a sulphuric acid surface reflects the chains better than a glass surface covered with oxides. Correspondingly, phosphine may be adsorbed on the oxide coated wall yielding a surface which is much more effective in the termination of chains than the oxides alone. The critical explosion pressure is thus raised. In this connection it may be pointed

out that the curve obtained by plotting explosion pressure ag phosphine pressure resembles an adsorption isotherm (Fig. 1). An observation supports this view. After a series of experiments had carried out with phosphine the tube had to be pumped out for an un long time before the explosion pressure fell to its original value.

TABLE III.

Pressure of PH_3.	Time * for Explosion. (Sec.)	Pressure of PH_3.	Time for Explosion. (Sec.)
0·0	5·0	0·0	6·0
0·1	14·0	0·5	19·2
0·2	18·4	0·9	32·0
0·5	31·4	1·3	28·0
2·2	58	2·0	48·0
5·0	75	2·6	61
7·5	72·4	3·0	67
10·0	75	3·7	72
15·0	72	4·8	86
		6·5	87
		10·0	94

one experiment when pumping out normally required two min the process had to be carried on for thirty minutes to regain nor conditions.

If the effect is due to inhibition in one of the forms suggested ab it is all the more surprising since phosphine itself is spontaneo inflammable in oxygen. Two series of experiments are recorded in Table III. to show the magnitude of the effect.

Pressure of Phosphorus. (mm.)	Time for Explosio
0	1 min. 40 secs
0·007	1 ,, 22 ,,
0·025	0 ,, 51 ,,

The addition of phosphorus vapour to phosphine *reduces* the lower critical explosion pressure of phosphine as is shown here.

These phenomena are being investigated in more detail in order ascertain what light they may ultimately throw on the phenomena the low pressure oxidation of phosphorus and of phosphine.

* This is the time required for oxygen to leak through a capillary into t reaction tube.

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INERT GAS EFFECTS IN CHAIN REACTIONS.

INERT GAS EFFECTS IN CHAIN REACTION

By H. W. Melville.

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In certain chain reactions, particularly thermal oxidations, in which wall deactivation is prominent, it has been shown that the addition of inert gases increases the rate of oxidation. This phenomenon is explained by Semenoff [1] on the assumption that the inert gas hinders the diffusion of the chains to the walls, postpones deactivation and thereby increases the length of the chains. It was shown by Semenoff that the increase in chain length can be represented by the factor

$$1 + p_X/(p_R + p_{O_2})$$

where p_X, p_R and p_{O_2} are the pressures of inert gas, oxidisable substance and ogygen respectively. This expression was derived from the simple

[1] *Z. Physik.*, **47**, 109, 1927; *Z. physikal. Chem.*, **2B**, 161, 1929.

assumption that the mean free path of the chains in the gas mixture is inversely proportional to the total pressure. Later work on the phosphorus-oxygen reaction [2] revealed that this was only a first approximation, the second approximation factor being

$$1 + \mu p_X/(p_R + p_{O_2})$$

where μ is a constant and is inversely proportional to the diffusion coefficient of the chains through the gas mixture.

It has now been found that this second approximation holds valid for a number of chain reactions. The object of the present note is to point out some regularities in the values of μ in different reactions and to show that these regularities are in agreement with the theory so far as it has been developed.

The determination of the value of μ may be carried out in two different ways. In the first, the acceleration of the stable chain reaction velocity may be measured. If R_X and R_0 are the rates with and without inert gas present then μ is given by

$$\mu = \frac{R_X - R_0}{R_0} \frac{p_R + p_{O_2}}{p_X}. \quad . \quad . \quad . \quad (1)$$

In the second method μ may be obtained by measuring the lowering of the lower oxidation limit upon the addition of inert gas. In these circumstances

$$p'_R p'_{O_2} = p_R p_{O_2}(1 + \mu p_X/(p_R + p_{O_2})) \quad . \quad . \quad (2)$$

where p' denotes pressures in absence of inert gas.

The Experimental Data.

The available experimental data for six oxidation reactions are collected in Table I.

TABLE I.—Reaction.

Inert Gas.	$H_2 - O_2$.		$CH_4 - O_2$.	$PH_3 - O_2$.	$H_2S - O_2$.	$CS_2 - O_2$.	$P_4 - O_2$.
He . .	0·15	2·3	—	—	—	—	0·13
Ne . .	—	—	—	—	—	—	0·20
A . .	1·16	7·3	0·8	0·9	0·59	0·64	0·46
N_2 . .	2·35	5·1	1·2	0·3	0·44	0·42	0·37
CO_2 . .	2·4	—	1·5	—	—	0·83	0·48
SO_2 . .	2·6	—	2·7	—	—	0·92	0·52
$CH_2(OEt)_2$.	3·0	—	—	—	—	—	—
N_2O . .	4·8	—	—	—	—	—	0·46
CCl_4 . .	5·6	—	3·4 *	—	—	—	0·84
$CHCl_3$.	6·9	—	3·0 *	—	—	—	0·84

With phosphine [3] and phosphorus [2] the lower limiting explosion pressures were determined by the usual methods at temperatures in the neighbourhood of 15° C. In the case of hydrogen [4] and methane [5]

[2] Melville and Ludlam, *Proc. Roy. Soc.*, **132A**, 108, 1931.
* I am indebted to Dr. H. W. Thompson for these values.
[3] Dalton and Hinshelwood, *Proc. Roy. Soc.*, **125A**, 294, 1929.
[4] Thompson, *Trans. Faraday Soc.*, **28**, 299, 1932; *cf.* also Horde and Thompson, *J. Chem. Soc.*, in the press.
[5] Thompson and Kearton, *J. Chem. Soc.*, 933, 1932.

chain centres in sufficient concentration to produce lower lim explosion pressures had to be introduced by means of an electric s The carbon disulphide explosions had to be initiated by a hot tun filament.[6] Similarly a hot filament was required for the hyd sulphide,[7] the gas mixture in both cases being at about 15° C.

μ for neon and argon in the phosphorus reaction was confirm experiments on the stable chain reaction below the lower limit.[8]

The second column under the $H_2 - O_2$ reactions shows the va μ calculated from the data of Gibson and Hinshelwood[9] on the s chain reaction above the upper limit. The available data are giv Table II. and the value of μ calculated from equation (1). Pres are in mm. Hg.

TABLE II.

Helium.				Nitrogen.			
$p_{H_2 + O_2}$.	p_{He}.	Increase in Rate.	μ.	$p_{H_2 + O_2}$.	p_{N_2}.	Increase in Rate.	
450	300	2·45	2·2	300	50	1·26	(1
450	500	3·91	2·6	300	100	2·40	4
300	300	1·75	(1·7)	300	150	3·33	4
300	500	3·29	2·3	300	200	4·76	5
		Average	2·3	300	250	6·17	6
						Average	5

Argon.				Water Vapour.			
$p_{H_2 + O_2}$.	p_A.	Increase in Rate.	μ.	$p_{H_2 + O_2}$.	p_{H_2O}.	Increase in Rate.	
300	100	2·84	(5·5)	300	50	1·4	(2
300	200	5·24	6·3	300	100	3·6	7
300	500	14·2	7·9	300	200	6·2	7
300	700	19·1	7·7			Average	7
		Average	7·3				

The value of μ does not remain constant but increases with Moreover, the μ's for all gases are considerably greater than those tained by Thompson at the lower limit. Had the values of μ decre with p_X deactivation by the inert gas would have been indicated. opposite tendency seems to point to the kinetics being rather complex than at the lower limit, the inert gas not wholly functio in the manner common to the other reactions in Table I.

The abnormally large value of μ for N_2O in the spark experim for the $H_2 - O_2$ reaction is probably due to the N_2O participating in reaction for when H_2 and O_2 are sparked in presence of N_2O ther appreciable reaction of the N_2O with H_2. In fact explosive combina of H_2 and N_2O can be brought about by means of a spark.

[6] Ritchie and others, *Proc. Roy. Soc.*, in the press.
[7] Ritchie, private communication.
[8] Melville and Ludlam, *Proc. Roy. Soc.*, **135A**, 315, 1932.
[9] *Proc. Roy. Soc.*, **119A**, 591, 1928.

The values for phosphine are possibly complicated by the fact that deactivation is simultaneously occurring with the inert gas effect. For instance, with argon μ decreases down to about 0·3 as the pressure of argon increases; and with nitrogen, although μ remains fairly constant the value appears to be much too low.

It is interesting to point out here that in the photochemical $H_2 - Br_2$ reaction at low pressures where wall deactivation becomes evident [10] the inert gas effect increases in the series He, H_2, O_2, HBr, Br_2, thus falling into line with the results of the oxidation reactions.

Discussion.

Thompson [5] has made the interesting suggestion that it may be possible to estimate the approximate mass and diameter of the chain carriers by a detailed study of the inert gas effect and so enable plausible reaction mechanisms to be verified. For example, to take an extreme case it might be possible to say whether one of the chain carriers in the oxidation of methane is a heavy peroxide or hydroxylated molecule compared with the highly mobile hydrogen atoms and hydroxyl radicals which are supposed to play an essential part in the $H_2 - O_2$ reaction.[11]

On inspection of Table I. the first striking fact is that the inert gas coefficients for the $H_2 - O_2$ reaction are consistently higher than those for any of the other reactions. In order to see how this comes about the approximate expression for μ may be considered. It has been shown [12] that μ is given by *

$$\mu = \frac{\sigma_{AX}^2(1/M_A + 1/M_X)^{-\frac{1}{2}}}{\sigma_{AM}^2(1/M_A + 1/M_M)^{-\frac{1}{2}}}$$

where σ_{AX} is the sum of the radii of A, the chain carrier and X, the inert gas; and σ_{AM} that of A and M the reaction mixture. The radius of A and of M will be a mean value owing to the existence of two chain propagators and of the two different molecules of the reaction mixture. Similarly M_A and M_M will be mean molecular weights. In spite of these complications, it will be assumed that in the $H_2 - O_2$ reaction $M_A = 1$ and $M_M = 2$ and σ_A is the radius of the hydrogen atom. Owing to the small value of σ_A, it will have a relatively small influence on the factor $\sigma_{AX}^2/\sigma_{AM}^2$ so that this will be mainly governed by σ_X/σ_M, which will become large when σ_X is large—this, in turn, making μ large. On the other hand when σ_A is comparable with σ_X and σ_M, as is probably the case with the other reactions, $\sigma_{AX}^2/\sigma_{AM}^2$ will not become so great as σ_M increases. For a similar reason, the range of values of μ from He to CCl_4 — 0·15 — 6·9 will therefore be much larger than is the case with the $P_4 - O_2$ reaction, 0·13 — 0·84.

Turning now to the mass factor in the equation for μ it is seen on substituting the values for M_A and M_M and supposing M_X large a value of 1·5 is obtained again tending to make μ high. With other reactions M_A, M_X and M_M are comparable so that the mass factor will approxi-

[10] Jost and Jung, *Z. physikal. Chem.*, **3B**, 83, 1929. *Cf.* also Kassel, *Homogeneous Gas Reactions*, p. 243.

[11] Bonhoeffer and Haber, *Z. physikal. Chem.*, **137**, 263, 1928.

[12] Melville, *Trans. Faraday Soc.*, **28**, 308, 1932.

* This equation is obtained from equations (2) and (11) in reference 12. The coefficient k in (11) is written out in full since k will vary according to the particular reaction being considered.

mate to unity but perhaps rising slightly above this value as M_X bec large.

Thus both factors for the $H_2 - O_2$ reaction give high values The contribution of the OH radical in the $H_2 - O_2$ reaction has neglected for the sake of simplicity. If OH is taken into consider it would produce slightly lower values of μ.

Another regularity may be observed in Table I., μ for argon, nitro carbon dioxide and sulphur dioxide decreases in the series H_2, CH_4, CS_2, P_4. That is, as the mass and diameter of the oxidisable mole increases there is a corresponding decrease in μ for any one inert Now the mass and diameter of A will probably be proportional to M, a of the chain propagators is supposed to be a highly reactive mole resulting from the oxidation of the combustible substance. Consequ it would be expected for any given inert gas the factor $\sigma^2_{AX}/\sigma^2_{AM}$ w decrease slightly in the series H_2 to P_4. For a similar reason the factor would also tend to decrease.

Thus the two regularities, larger and greater range of μ for th actions involving lighter molecules of the oxidisable substance is acco for by the approximate theory.

Summary.

The effect of foreign gases on six oxidation chain reactions is s marised and discussed, the reactions being the oxidation of H_2, C PH_3, H_2S, CS_2 and P_4. Certain regularities in the influence of t gases are pointed out and shown to be in agreement with theory so fa it has been developed. For instance, the inert gas has a greater acce tive influence on those reactions involving the oxidation of light molec The available experimental data would appear to indicate, on the b of these calculations, that the mass of the chain carrier molecules incre with the mass of the molecule of the combustible substance.

The author wishes to thank Dr. E. B. Ludlam for his interest in paper and the Carnegie Trustees for a scholarship during the tenu which this work was carried out.

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The Photochemistry of Phosphine.

BY H. W. MELVILLE.

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The Photochemistry of Phosphine.

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Within recent years the spectroscopy and the photochemistry of the hydrides of the non-metallic elements has been the subject of much study and the results explained with considerable success on the basis of the newer theories of photochemical reactions. In spite of the fact that the photochemistry of ammonia has attracted some attention, yet the investigation of the equally simple molecule of phosphine seems to have been entirely neglected. It is with the object of filling this gap in photochemistry that the present experiments have been undertaken.

The investigation naturally falls into three parts : (*a*) the absorption spectrum of phosphine, (*b*) the direct photochemical decomposition, (*c*) the photosensitised decomposition. Experimental data on the photo-oxidation are also of importance in view of the fact that the thermal oxidation of phosphine is a chain reaction.

In the present communication attention will be devoted to the photosensitised reactions, while the absorption spectrum and direct photo-reactions will, it is hoped, be dealt with in another paper.

The Photosensitised Decomposition.

Phosphine does not exhibit any absorption of visible or ultra-violet light until a wave-length of 230 $\mu\mu$ is reached,* therefore, it is at once evident that, in principle, the mercury photosensitised reaction may be conveniently studied. The general plan of the investigation included experiments corresponding to those which had already been carried out with ammonia. In addition, it became necessary to extend this scheme as certain outstanding points required elucidation and extension.

Apparatus.

The arrangement of the apparatus employed is shown in fig. 1. The reaction tube was a long spiral of silica tubing 5 mm. in bore surrounding a simple form of mercury arc lamp. The lamp consisted of a slightly inclined silica tube 15 cm. long and 1 cm. in diameter fitted with side tubes and mercury reservoirs as is shown in the figure. The lamp and spiral were fitted into a brass tank through which water rapidly flowed for cooling purposes. The

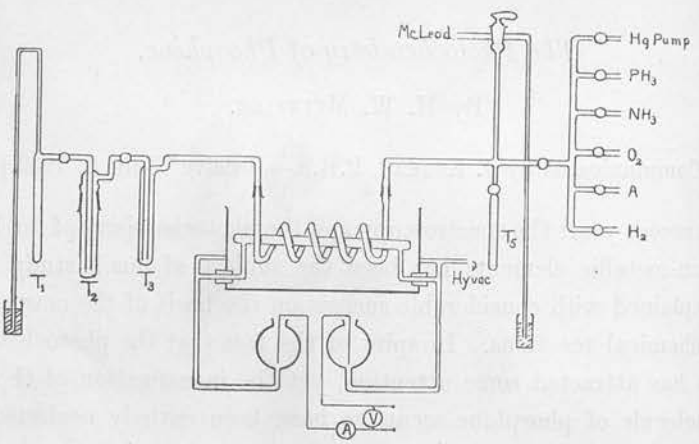

Fig. 1.

spiral was connected by means of silica-glass ground joints on the left side to a phosphine storage trap T_1, a trap T_2 for saturating the gas with phosphorus vapour, and T_3 which contained mercury in order to maintain the concentration of the vapour at a steady value in the spiral. T_3 was immersed in water contained in a vacuum flask. On the right side the spiral was attached (*a*) to storage bulbs and pipettes containing phosphine, ammonia, hydrogen, oxygen and argon ; (*b*) to a mercury manometer, McLeod gauge and a mercury vapour

* Melville, 'Nature,' vol. 129, p. 546 (1932).

pump. Suitable liquid air traps and small reservoirs were connected to this part of the apparatus in order to facilitate the handling of the various gases used in these experiments.

During the preliminary work the brass box was filled with a 2·5 per cent. aqueous solution of potassium bromide in order to make sure that all light of $\lambda < 240$ $\mu\mu$* was filtered out from the radiation of the mercury lamp. In this case the solution was cooled by a coil of lead pipe in which a current of water circulated. After several hours' exposure the KBr was markedly decomposed. Later experiments showed that with unfiltered light from a water cooled arc the photosensitised was at least 100 times faster than the direct decomposition.

When it was found that the rate of the reaction depended to some extent on the surface-volume ratio of the reaction tube the arrangement of lamp and reaction tube was changed. A vertical water cooled lamp and interchangeable cylindrical insolation vessels were substituted for the horizontal lamp.

Since the experimental procedure varies with the type of experiment, details of the methods employed are most conveniently given with the numerical results.

Materials.

The phosphine was prepared from phosphonium iodide and potassium hydroxide, passed over soda lime, calcium chloride and phosphorus pentoxide collected in a liquid air trap after which it was fractionally distilled, the middle portion of the distillate being used. Ammonia was obtained by heating ammonium chloride and soda lime, dried with soda lime and fractionally distilled with solid carbon dioxide.

Products of Decomposition.

The first point to be settled about the photosensitised reaction is the nature of the end products. With the experimental arrangement described above using pressures of phosphine from 0·05 mm. up to 760 mm. an exposure of a few minutes or even seconds (at high phosphine pressures) sufficient to yield an amount of gas, non-condensible in liquid air, giving a pressure of about 0·1 mm. This gas could only be hydrogen. After a large number of exposures it was observed that the rate of decomposition gradually fell off and simultaneously a brown deposit was formed on the walls of the reaction tube. This

* 'Z. Elektrochem.,' vol. 35, p. 702 (1929).

brown deposit was most probably red phosphorus or a phosphorus hydride since it was easily removed by heating or by washing with bromine water.

If phosphine is decomposed according to the equation $4PH_3 = P_4 + 6H_2$ then the pressure of hydrogen produced should be 1·5 times that of the phosphine decomposed. Phosphine was introduced into the apparatus at a pressure which could be conveniently measured by the McLeod gauge, it was illuminated for a suitable length of time (in this case about 10 minutes, with 30 volts and 4 amps. in the arc) and the pressure again measured ; the phosphine was then condensed out with liquid air in order to measure the pressure of the hydrogen. From these pressure readings, after making a small correction due to the fact that phosphine has a small vapour pressure at liquid air temperatures. it was then possible to calculate the percentage hydrogen produced. Table I gives a set of typical results.

Table I.

Initial pressure of PH_3 (mm.).	Total pressure after illumination.	Pressure of H_2 (mm.).	Percentage H_2 produced.
0·0550	0·0605	0·0200	92
0·0985	0·1055	0·0230	96
0·0645	0·0720	0·0245	95
0·1710	0·1925	0·0745	94
0·1015	0·1125	0·0390	93
0·0520	0·0585	0·0225	98
		Average	95

The average of 95 per cent. of the theory thus pointed to the conclusion that nearly all the phosphine decomposed formed phosphorus and hydrogen. The small deficiency in the amount of hydrogen is due, as will be shown later, to the clean up of part of the hydrogen on the walls of the insolation tube. Whether phosphorus vapour is first produced in the decomposition is not known, since under the influence of light from the mercury lamp the vapour is transformed into red phosphorus.

In spite of the fact that red phosphorus appears as the final product of the reaction, it was important to find if the addition of phosphorus vapour caused any decrease in the rate owing to the absorption of the 253·6 $\mu\mu$ line of the mercury spectrum. A piece of yellow phosphorus was placed in T_2 which was kept at — 80° C. while phosphine was passed into the spiral at about 2 mm. pressure. An exposure was made, the phosphine condensed out and the

pressure of hydrogen determined. After pumping out and refilling the spiral with the same pressure of phosphine, T_2 was warmed up to 15° (vapour pressure of yellow phosphorus 0·026 mm.) and a trap on the right side of the spiral cooled to −80° so that a constant stream of phosphorus vapour passed through the spiral. Experiments were made alternately with and without phosphorus vapour when it was found that only a slight diminution in rate occurred, *e.g.*, from 0·0250 mm./min. to 0·0245, 0·0295 to 0·0285, 0·0300 to 0·0295. The small influence of the phosphorus is, no doubt, due to the high absorption coefficient of the mercury vapour for the resonance line compared with that of phosphorus vapour; for example,* with a mercury vapour pressure of 0·001 mm. 95 per cent. of the resonance line is absorbed in a layer of vapour 2 cm. thick.

Effect of Hydrogen.

It is well known that molecular hydrogen is a paticularly efficient deactivator of excited ($2\,^3P_1$) mercury atoms,† so that it would be expected that, as hydrogen accumulates in the phosphine during decomposition, the reaction velocity will fall off even if the pressure of phosphine is maintained at a constant value. This is clearly illustrated in fig. 2, and it is to be noted that the inhibition by hydrogen is more marked with small phosphine pressures. In order to discuss the matter quantitatively, it will be convenient at this point to propose a simple mechanism for the reaction and to find how far this mechanism can account for the experimental data. The rate of decomposition is given by

$$R = -\frac{d[PH_3]}{dt} = k_1[Hg'][PH_3], \qquad (1)$$

where k_1 is a constant, Hg′ denotes the excited mercury atom in the $^3P_1$ state. Since the system is in a stationary state, then the following relationship exists

$$\frac{d[Hg']}{dt} = K - k_1[Hg'][PH_3] - k_2[Hg'][H_2] - k_3[Hg'] = 0, \qquad (2)$$

or

$$[Hg'] = \frac{K}{k_1[PH_3] + k_2[H_2] + k_3}, \qquad (3)$$

where K is proportional to the intensity of the illumination and the concentration of the mercury vapour. The third term of (2) takes into account

* Gaviola, 'Phil. Mag.,' vol. 6, p. 1154 (1928).

† Stuart, 'Z. Physik,' vol. 32, p. 262 (1925); Zemansky, 'Phys. Rev.,' vol. 36, p. 919 (1930).

deactivation of Hg′ by H_2, while k_3 is the rate at which Hg′ reverts to the 1^1S_0 state by radiation or by any other process which is independent of PH_3 and H_2, *e.g.*, wall deactivation. Deactivation by radiation is probably the most important factor in this term owing to the short life (10^{-7} seconds) of the excited atom.

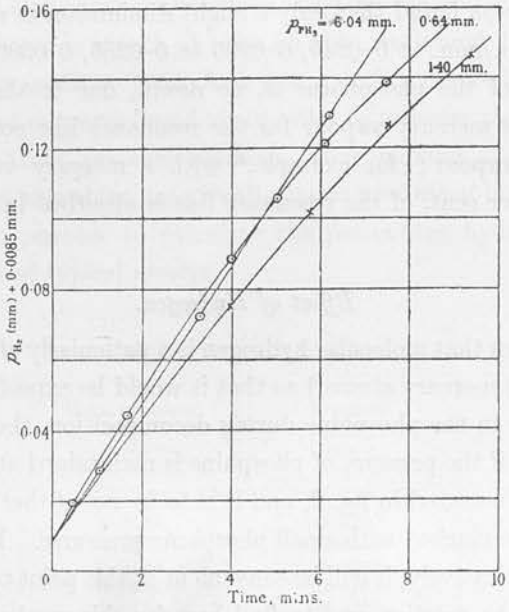

FIG. 2.—The inhibitory effect of hydrogen is shown by the decomposition curves becoming concave to the time axis as p_{H_2} increased. The curvature is greater the smaller the pressure of phosphine. The small variation in initial rate of reaction is due to variation in the intensity of the mercury lamp. 0·0085 mm. is the vapour pressure of PH_3 at −183° C.

From equations (1) and (3)

$$1/R = 1/K\left(1 + \frac{k_2[H_2] + k_3}{k_1[PH_3]}\right), \qquad (4)$$

and therefore if 1/R is plotted against $[H_2]$ for a constant $[PH_3]$ a straight line should be obtained. Further, if R_0 and R_H are the values of R at the beginning of the reaction and after the hydrogen has accumulated, then from (4)

$$\frac{R_0 - R_H}{R_H} = \frac{k_2[H_2]}{k_1[PH_3] + k_3}, \qquad (5)$$

whereby it is then possible to calculate k_2/k_3 if k_1/k_3 is known. The ratio k_1/k_3 is obtained by the method detailed on p. 384.

The horizontal lamp and spiral were used, the phosphine pressure being 4·40 mm. and exposure time 2 minutes. Tables II and III give the record of a typical series of experiments.

Table II.

H_2 added (mm.).	Total p_{H_2} after experiment.	R mm./2 minutes.	Mean p_{H_2} during experiment.
0·000	0·0225	0·0225	0·0112
0·0435	0·0620	0·0185	0·0530
0·0775	0·0935	0·0106	0·0855
0·1080	0·1210	0·0130	0·1145
0·1405	0·1500	0·0095	0·1455

Table III.

p_{H_2}.	R.	k_2/k_3.	p_{H_2}.	R.	k_2/k_3.
0·00	0·0233	—	0·08	0·0163	32·5
0·02	0·0216	23·9	0·10	0·0145	36·7
0·04	0·0200	25·0	0·12	0·0125	43·5
0·06	0·0180	29·8	0·14	0·0103	54·5

The results in Table III were obtained by plotting the mean p_{H_2} against R in Table II, and extrapolating back to R_0. p_{H_2} and R of Table III are then read off from the curve and k_2/k_3 calculated by means of (5). Fig. 3 shows R and 1/R plotted against p_{H_2}. As is seen, (*a*) from fig. 3 the plot of 1/R against

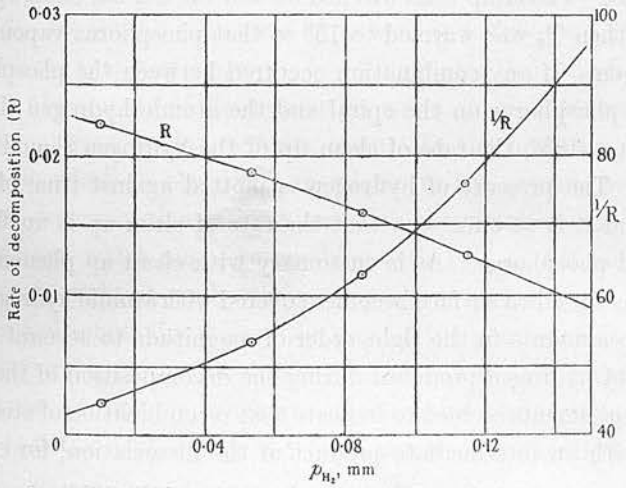

FIG. 3.—The reciprocal of the rate of decomposition of PH_3 is not proportional to p_{H_2} as would be expected theoretically.

p_{H_2} is not a straight line but a curve convex to the p_{H_2} axis, and (*b*) from Table III, k_2/k_3 does not remain constant but increases with p_{H_2}. That is, the inhibitory effect of hydrogen is greater than that predicted on the assumption that deactivation alone is responsible for the decrease in the rate of decomposition.

It might be suggested that this additional effect is due to the hydrogen atoms produced by collisions between excited mercury atoms and H_2, recombining with the red phosphorus deposited on the walls of the reaction vessel. There are, in the literature two records of the action of atomic hydrogen on yellow phosphorus. Langmuir* found that although a hot (1200° K.) tungsten filament dissociates PH_3 into yellow phosphorus (which is deposited on the walls of the tube) and hydrogen, when the filament was heated to a higher temperature the atomic hydrogen, produced by impact of H_2 on the tungsten surface, is able to recombine with the phosphorus to regenerate phosphine. Similarly Bonhoeffer† found that atomic hydrogen produced in a Wood's tube readily reacts with white phosphorus to give PH_3, but in addition, a brown iridescent film was formed in the neighbourhood of the phosphorus. It is of importance to note that this film was apparently unattacked by atomic hydrogen. If the brown deposit is similar to that obtained in the photosensitised decomposition of phosphine, then atomic hydrogen ought not to retard the reaction in this manner.

However, experiments were made to find if, *under the experimental conditions employed in this work*, there was any reaction between phosphorus and atomic hydrogen produced photochemically. The method employed consisted in admitting hydrogen to the silica spiral with trap T_3 at 15°, T_2 at −80°, and T_5 at −183°. The lamp was switched on and the normal clean up of hydrogen measured, then T_2 was warmed to 15° so that phosphorus vapour mixed with the hydrogen. If any combination occurred between the phosphorus vapour or the red phosphorus on the spiral and the atomic hydrogen then, owing to T_5 being at −183°, the rate of clean up of the hydrogen should be markedly increased. The pressure of hydrogen is plotted against time of illumination in fig. 4 and it is at once seen that the rate of clean up is unaffected by the presence of phosphorus. As is customary with clean up phenomena the rate decreases as the silica surface becomes covered with atomic hydrogen. The rate of clean up amounts to the right order of magnitude to account for the slight deficiency of hydrogen produced during the decomposition of the phosphine.

These experiments seemed to indicate that recombination of atomic hydrogen occurred with an intermediate product of the dissociation, for example, PH_3

* 'J. Amer. Chem. Soc.,' vol. 34, p. 1310 (1912).

† 'Z. Phys. Chem.,' vol. 113, p. 199 (1924).

or PH radicles. The existence of PH_2 is not known, but apparently PH radicles can exist in flames* and discharge tubes.† Since these radicles probably have only a comparatively short life, it was necessary to devise an experiment whereby atomic hydrogen could be produced in the reaction tube independently of, but simultaneously with the photo-dissociation of the phosphine molecule, and to observe whether the rate of dissociation is decreased.

It is probable that the initial process in the photosensitised decomposition of PH_3, $Hg(2\,^3P_1) + PH_3 = PH_2 + H + Hg(1\,^1S_0)$ is similar to the direct

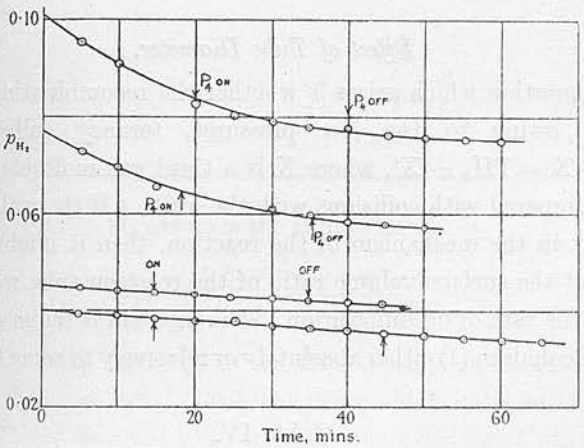

FIG. 4.—The clean up of the hydrogen is not affected by the presence of phosphorus vapour, hence no phosphine is formed.

reaction, $h\nu + PH_3 = PH_2 + H$. On the strength of this assumption, the basis of the idea for testing the above hypothesis is as follows. Phosphine is mixed with a large excess of hydrogen and illuminated, (*a*) with light from a zinc spark and the amount of decomposition noted, (*b*) simultaneously with a zinc spark and a water-cooled mercury lamp. In the first case, the excess hydrogen has no effect on the direct reaction; in the second, however, the photosensitised decomposition is inhibited with the simultaneous production of atomic hydrogen which ought to combine with PH_2 or PH and so retard the dissociation brought about by the zinc spark.

Owing to experimental limitations the rate of the photosensitised reaction was quite comparable with the direct reaction. The latter could not be increased because of the low pressure of phosphine and consequent small absorption of radiation; the spark also could not be conveniently increased in

* Ludlam, 'Nature,' vol. 128, p. 271 (1930).

† Pearse, 'Proc. Roy. Soc.,' A, vol. 129, p. 328 (1930).

intensity as it was already consuming 1 amp. at 4000 volts. Separate exp ments were therefore made with arc and spark and the total amount of hydro produced compared with that from the simultaneous illumination. Inspect of Table IV shows that there is in every case a much smaller amount hydrogen obtained with simultaneous illumination. In order to prove t point beyond doubt, the two experiments recorded at the bottom of Table show that the effect is not observed if hydrogen is absent. A 2-cm. silica tu was used with the arc and spark on either side.

Effect of Tube Diameter.

The next question which arises is whether the recombination occurs at t walls, since owing to the low pressures, ternary collisions, such a $PH_2 + H + X = PH_3 + X'$, where X is a third gas molecule, are extrem infrequent compared with collisions with the walls. If the walls do play som essential part in the mechanism of the reaction, then it might reasonably supposed that the surface/volume ratio of the reaction tube would have som influence on the rate of decomposition. The problem is reduced to finding t value of k_1 of equation (1) either absolutely or relatively to some fixed coefficien *e.g.*, k_2.

Table IV.

p_{PH_3} (mm.).	$p_{PH_3} + p_{H_2}$ (mm.).	p_{H_2} after exposure.	p_{H_2} produced from PH_3.		Source of illumination.
0·0865	0·1360	0·0720	0·0225	0·0415	Arc.
0·0850	0·1345	0·0685	0·0190		Spark.
0·0850	0·1335	0·0810	0·0325		Spark + arc.
0·0575	0·1455	0·0970	0·0050	0·0165	Arc.
0·0560	0·1465	0·1020	0·0115		Spark.
0·0535	0·1405	0·0935	0·0065		Spark + arc.
0·0555	0·1445	0·0975	0·0085		Spark + arc.
0·0570	0·1470	0·0985	0·0105	0·0155	Spark.
0·0575	0·1455	0·0930	0·0050		Arc.
0·0555	0·1110	0·0695	0·0140	0·0215	Arc.
0·0570	0·1110	0·0615	0·0075		Spark.
0·0570	0·1145	0·0735	0·0150		Spark + arc.

Table IV—(continued).

p_{PH_3} (mm.).	$p_{PH_3} + p_{H_2}$ (mm.).	p_{H_2} after exposure.	p_{H_2} produced from PH_3.		Source of illumination.
		HYDROGEN ABSENT.			
0·0550	—	—	0·0170	0·0290	Arc.
0·0570	—	—	0·0120		Spark.
0·0585	—	—	0·0300		Spark + arc.
0·0580	—	—	0·0190	0·0310	Arc.
0·0585	—	—	0·0120		Spark.
0·0585	—	—	0·0300		Spark + arc.

If $[H_2] = 0$, equation (4) assumes the simple form

$$1/R = 1/K\left(1 + \frac{k_3}{k_1[PH_3]}\right), \qquad (6)$$

so that the ratio of the intercept to the slope of the line obtained by plotting $1/R$ against $1/[PH_3]$ is k_1/k_3. This equation which indicates how R varies with $[PH_3]$ will only be valid provided that the pressure of phosphine is low enough to prevent pressure broadening of the absorption line of mercury vapour. This was ensured in these experiments by working with pressures below 10 mm. Tubes of 2, 1, and 0·5 cm. bore were used, the results are given in Tables V–VII and the data in Table VII plotted in fig. 5. Correction is

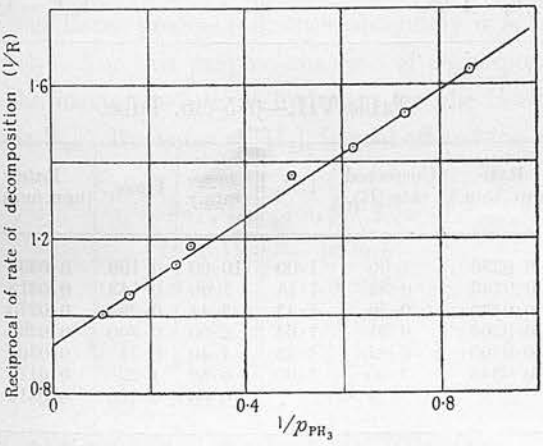

FIG. 5.—The reciprocal of the rate of decomposition of PH_3 is proportional to $1/p_{PH_3}$ as is to be expected on the simple theory of the effect.

made for the deposition of red phosphorus on the walls. Since the value k_1/k_3 increases with increasing diameter of tube, it would appear that recombination of the products is facilitated by larger surface/volume ratios and therefore that recombination occurs on the walls.

Table V.—2-cm. Tube.

p_{PH_3} (mm.).	$1/p_{PH_3}$.	Rate, (mm./min.)	Corrected rate (R).	1/R.	p_{PH_3} (mm.).	$1/p_{PH_3}$.	Rate (mm./min.)	Corrected rate (R).	1/R.
10·00	0·100	0·0425	1·00	1·00	10·00	0·100	0·0380	1·00	1·00
1·26	0·80	0·0300	0·75	1·33	1·80	0·56	0·0280	0·80	1·25
0·62	1·61	0·0245	0·66	1·52	0·56	1·79	0·0220	0·67	1·49
0·36	2·78	0·0170	0·50	2·00	0·32	3·12	0·0160	0·52	1·92
0·20	5·00	0·0140	0·45	2·22	0·20	5·00	0·0105	0·36	2·78
10·00	0·100	0·0285	1·00	1·00	10·00	0·100	0·0270	1·00	1·00
$k_1/k_3 = 2·70$.					$k_1/k_3 = 2·7$.				

Table VI.—1-cm. Tube.

p_{PH_3} (mm.).	$1/p_{PH_3}$.	Rate (mm./min.)	Corrected rate (R).	1/R.	p_{PH_3}. (mm.)	$1/p_{PH_3}$.	Rate (mm./min.)	Corrected rate (R).	1/R.
5·16	0·194	0·0360	1·00	1·00	10·60	0·094	0·0285	1·00	1·00
3·60	0·278	0·0330	0·91	1·10	5·24	0·190	0·0245	0·86	1·16
1·90	0·525	0·0285	0·79	1·27	2·20	0·455	0·0210	0·74	1·35
0·96	1·04	0·0230	0·64	1·56	1·16	0·86	0·0190	0·67	1·49
$k_1/k_3 = 1·60$.					$k_1/k_3 = 1·56$.				

Table VII.—0·5-cm. Tube.

p_{PH_3} (mm.).	$1/p_{PH_3}$.	Rate (mm./min.)	Corrected rate (R).	1/R.	p_{PH_3} (mm.).	$1/p_{PH_3}$.	Rate (mm./min.)	Corrected rate (R).	1/R.
10·00	0·100	0·0330	1·00	1·00	10·00	0·100	0·0335	1·00	1·00
4·22	0·237	0·0290	0·88	1·14	7·00	0·143	0·0315	0·95	1·06
1·62	0·62	0·0230	0·70	1·43	3·44	0·290	0·0270	0·83	1·21
1·16	0·86	0·0205	0·61	1·64	2·00	0·500	0·0230	0·72	1·39
2·40	0·417	0·0295	0·87	1·15	1·40	0·71	0·0205	0·64	1·57
10·00	0·100	0·0345	1·00	1·00	0·82	1·22	0·0175	0·56	1·79
					10·00	0·100	0·0315	1·00	1·00
$k_1/k_3 = 1·15$.									

Comparison of the PH_3 *and* NH_3 *Reactions.*

It is interesting to compare the phosphine results with those of ammonia obtained by Mitchell and Dickinson* who suggested a mechanism involving excited ammonia molecules. The existence of these molecules is rendered exceedingly improbable by Bonhoeffer and Farkas' work† on the photochemistry of ammonia. If the mechanism suggested in equations (1) and (2) also holds for the decomposition of ammonia, then from Mitchell and Dickinson's results the value of k_1/k_3 may be readily obtained and amounts to 0·20 mm.$^{-1}$. Whether k_1/k_3 depends on the diameter of the insolation tube is not yet known, but it is evident that the phosphine reaction, according to these calculations, is about ten times as fast as the ammonia decomposition. This result was confirmed by a direct comparison using pressures of ammonia and phosphine of 6 mm. in a cylindrical tube 2 cm. in diameter when 0·00115 mm. of N_2 and H_2 were produced per minute from NH_3 and 0·0118 mm./min. of hydrogen from PH_3.

It is impossible at present to find if this larger yield is due to the greater efficiency of PH_3 as a deactivator of Hg 2 $^3P_1$, or to the reactions subsequent to the dissociation of the PH_3 molecule being more efficient than the corresponding ammonia reactions. The effect may be due to both factors.

Another important calculation concerning the ammonia reaction may be made from the results of Mitchell and Dickinson. From equation (5) if $[H_2]_{\frac{1}{2}}$ is the pressure of hydrogen required to reduce R to $\frac{1}{2}R_0$ then

$$k_2 [H_2]_{\frac{1}{2}} = k_1 [NH_3] + k_3. \qquad (7)$$

The slope of the line obtained by plotting $[H_2]$ against $[NH_3]$ gives k_1/k_2, *i.e.*, k_1 is obtained relatively to the rate of deactivation of Hg 2 $^3P_1$ by H_2. Since the efficiency of this latter process is known absolutely it is then possible to obtain k_1 absolutely. For this purpose the rate of decomposition of NH_3 is plotted against the mean pressure of hydrogen for the interval concerned; extrapolation gives R_0. The value of $[H_2]_{\frac{1}{2}}$ is read off and the following results obtained:—

p_{NH_3}. (mm.)	p_{H_2} for $\frac{1}{2}R_0$. (mm.)
0·96	0·026
1·88	0·055
3·22	0·077
5·06	0·140

* 'J. Amer. Chem. Soc.,' vol. 49, p. 1487 (1927).
† 'Z. phys. Chem.,' vol. 134, p. 337 (1928).

In calculating their results Mitchell and Dickinson assumed that [H was independent of [NH_3]—a supposition which is incorrect as is shown the table above. From these data $k_1/k_2 = 0{\cdot}028$. Thus the ammo decomposition would appear to be much less efficient than quenching hydrogen. k_1 and k_2 are, however, composite factors and are given by equation

$$\frac{k_1}{k_2} = \frac{\alpha\sigma_1^2\,(1/M_{Hg} + 1/M_{NH_3})^{\frac{1}{2}}}{\sigma_2^2\,(1/M_{Hg} + 1/M_{H_2})^{\frac{1}{2}}},$$

where σ_1 and σ_2 are the *effective* collision radii of the partners Hg and N and Hg and H_2, M denotes the molecular weight. α is a factor which deno the number of ammonia molecules decomposed per collision which is effecti in deactivating the excited mercury atom. Zemansky* has recently carri out a series of very careful experiments on the quenching of mercury res nance radiation from which it is possible to obtain values for σ. For N $\sigma_1^2 = 2{\cdot}94 \times 10^{-16}$ cm.^{2} and H_2, $\sigma_2^2 = 6{\cdot}01 \times 10^{-16}$ cm.^{2}. Inserting the values in equation (8) $\alpha = 0{\cdot}162$. The corresponding result of Warbur for the direct decomposition, *viz.*, $\gamma = 0{\cdot}25$ (γ = quantum efficiency) wou indicate that, if the collision between Hg 2 $^3P_1$ and NH_3 resulting in deactivati of the mercury atom also results in fission of the NH_3 into NH_2 and H then, view of the correspondence between γ and α the processes succeeding t elementary decomposition may possibly be identical.

Another interesting point of resemblance of the photosensitised reactio lies in the fact that 1/R is plotted against the pressure of hydrogen, curv convex to the abscissæ are obtained as is the case with phosphine. He again hydrogen would appear to exert an inhibitory effect on the reactio which is greater than that calculated on the assumption of simple deactivatio The explanation is probably the same and, furthermore, the low quantu yield is possibly due to wall recombination of the primary products o dissociation.

As has been shown above the phosphine reaction is about 10 times as fas as the ammonia reaction hence from equation (7) it is at once seen that th inhibition by hydrogen is much less marked. Small pressures of phosphin have to be used in order to obtain accurately measurable effects; this, i turn, introduces the difficulty that the phosphine pressure diminishes durin an exposure and with it the reaction velocity. However, extended attempt

* 'Phys. Rev.,' vol. 36, p. 919 (1930).

† SitzBer. preuss. Akad. Wiss., p. 741 (1911); compare also Wiig and Kistiakowsk 'J. Amer. Chem. Soc.,' vol. 54, p. 1906 (1932).

were made but the results were so variable that little use could be made of them to calculate k_1/k_2.

The Photosensitised Oxidation.

Phosphine and oxygen inflame spontaneously between certain limiting pressures,* so that photochemical experiments must be confined to pressures either above or below the explosion limits. The experiments described below are concerned with pressures at or below the lower limit. First of all, it was thought that by adding oxygen to the phosphine the rate of decomposition would be increased since the products of the primary dissociation would be oxidised before they had an opportunity to recombine. The experimental procedure was as follows: phosphine was admitted to the reaction tube and the pressure measured on the McLeod gauge; it was then condensed out with liquid air and oxygen admitted to a known pressure such that the total pressure of PH_3 and O_2 was below the lower limit when the PH_3 evaporated. The exposure was made and the pressure of the gas not condensable by liquid air determined, this gas was then pumped off and the pressure exerted by the residual phosphine (after evaporation) recorded. Small corrections were applied owing to the volatility of the phosphine at −183°. Inspection of Table VIII shows that a considerable increase in reaction velocity is obtained in the presence of oxygen thus lending apparent support for the recombination

Table VIII.

Initial p_{PH_3}.	p_{O_2} added.	p of uncondensed gas after experiment.	p_{PH_3} decomposed.
0·0750	0·0285	0·0340	0·0280
0·0760	—	—	0·0150
0·0885	0·0710	0·0795	0·0605
0·0885	—	—	0·0070
0·0865	0·0220	0·0390	0·0405
0·0885	—	—	0·0070
0·0915	0·0890	0·0670	0·0525
0·0885	—	—	0·0160

hypothesis. The curious anomaly is that the pressure of uncondensable gas is about equal to that of the oxygen. Since oxygen accelerates the reaction

* Dalton and Hinshelwood, 'Proc. Roy. Soc.,' A, vol. 125, p. 294 (1929); Dalton, *ibid.*, A, vol. 128, p. 263 (1930).

it must be used up and, further, any oxide that might be formed is involat at −183° so that the residual gas will probably be hydrogen. Therefo the scheme of the reaction may be amended : the oxygen attacks the produ of dissociation, forming oxides of such an energy content that they are ab to activate phosphine or oxygen molecules which initiate a stable chain reacti between the residual PH_3 and O_2. If this supposition is correct then t subsequent addition of argon to the PH_3–O_2 mixture ought to increase the re still further, precisely in the same way as argon accelerates* the stable cha oxidation of phosphorus. The data given in Table IX show that the surmi is correct. Argon does not accelerate the reaction in absence of oxygen. I is therefore not possible to say whether wall recombination is retarded b oxidation owing to the intervention of the chain mechanism.

Table IX.

Initial p_{PH_3}.	p_{O_2}.	p_A.	p uncondensable gas.	p_{PH_3} decomposed.
0·0565	—	—	—	0·0115
0·0500	0·0375	—	0·0275	0·0245
0·0545	0·0425	0·0940	0·1215	0·0350
0·0675	—	—	—	0·0125
0·0675	0·0310	—	0·0385	0·0365
0·0660	0·0325	0·0900	0·1355	0·0455
0·0590	—	—	—	0·0135
0·0610	0·0325	—	0·0420	0·0295
0·0590	0·0325	0·1170	0·1520	0·0435

Effects at the Lower Limit in PH_3–O_2 *Mixtures.*

When a PH_3–O_2 mixture below the lower limit is illuminated by a mercury lamp, Hinshelwood and Clusius† found that on compression explosion took place at a much lower pressure than the normal unilluminated mixture. The effect, however, is not permanent but decays slowly, the original explosion pressure being reached. On further investigation the phosphine proved to be the origin of the effect and Hinshelwood and Clusius suggested that the phosphine molecule became activated by absorption of light ; the presence of this activated molecule of long life produces the lowering of the limit. From the decay curves it was estimated that the active molecule could make as

* Melville and Ludlam, ' Proc. Roy. Soc.,' vol. 135, p. 315 (1932).

† ' Proc. Roy. Soc.,' A, vol. 129, p. 589 (1930).

many as 10^5 collisions with the walls before being deactivated. Since no excited or metastable molecule could undergo so many collisions with a wall without becoming deactivated, it was concluded that the molecule was active in virtue of its chemical unsaturation rather than its high energy content.

Now in the theory of the oxidation of phosphine* the concentration $[X_0]$ of one of the chain propagators is given by

$$[X_0] = \frac{k_1 k_2 [O_2] F(c) + k_1 K . F(c)}{(1-\alpha) k_2 k_3 [PH_3][O_2] + k_2 K [O_2] + k_3 K [PH_3] + K^2} \qquad (9)$$

where k_1, k_2 and k_3 are velocity coefficients and K the rate of deactivation of X_0 at the walls, $F(c)$ is the rate of production of chain centres. The condition for explosion is that $[X_0] = \infty$ or that the denominator of (9) is zero. $F(c)$ does not appear in the denominator hence the explosion pressure ought to be independent of the rate of production of chain centres, therefore, the presence of active molecules produced photochemically should not alter the explosion limit. From (9) then, at the explosion limit

$$[PH_3][O_2] = K' \times \text{constant},$$

K' expressing the efficiency of deactivating collisions of X_0 with the walls. A variation in the condition of the walls may consequently alter the explosion limit.

Before proceeding, the question which required to be settled was whether the effect was due to the walls in spite of Hinshelwood and Clusius' demonstration that illumination of the tube itself did not change the explosion pressure.

For this purpose two similar silica tubes provided with graduated scales and mercury reservoirs were connected together by a short length of tubing having a tap in the middle. This apparatus was connected to sources of PH_3 and O_2, pumps, etc. Phosphoric acid was used to coat the insides of the illumination tubes in order to maintain constant surface conditions. A hot mercury arc was employed for most experiments, although a water-cooled lamp was also used but owing to the intense resonance radiation it had to be placed at a considerable distance from the tube in order to avoid excessive photo-oxidation. No filters were employed. Let A and B (in which the explosion pressures are determined) be the two tubes. The principle of the method consists in illuminating a PH_3–O_2 mixture in A and transferring immediately afterwards to B where the explosion pressure is measured. If the effect is a surface phenomenon, then the explosion pressure should be identical with that of a similar

* Dalton and Hinshelwood, *loc. cit.*

unilluminated mixture, because the active surface remains behind in A. On the other hand, if the active material is present in the gas it should produce in B a diminished explosion pressure.

Hinshelwood and Clusius' experiments were repeated; for example, after 4 minutes' illumination of B the explosion pressure fell from 19·5 to 17· (arbitrary) units. On allowing the illuminated mixture to stand for 4 minutes in B and also in contact with the tubes connecting A and B, the explosion pressure had risen to 17·3. Since the time of transference was about 1 seconds no appreciable loss of active product would occur in this interval.

In one experiment when the mixture was illuminated in A and the explosion pressure determined in B the latter amounted to 22·1 units. Without illumination it was 22·2. In two succeeding experiments the respective values were 20·5 and 20·5; 22·0 and 21·6. There seemed no doubt therefore, that the alteration of surface conditions was responsible for the greater explosibility of the illuminated mixture.

Since the effect has its origin primarily in the phosphine molecule, one explanation would be that the PH_2 radicles or H atoms are adsorbed on the walls which then become less efficient in deactivating the chain propagators, the chain length thereby being increased and the explosion pressure consequently diminished. But it has been seen that in presence of oxygen the rate of decomposition of the phosphine is greatly increased. If this fact is taken into consideration with Frankenburger and Klinkhardt's extensive work* on the mercury photosensitised H_2–O_2 reaction, which proceeds initially by means of the ternary collision $H + H_2 + O_2 = H_2O + OH$, then it is most probable, in view of the comparatively low pressures (< 1 mm.) and therefore infrequency of ternary collisions, that the phosphorus containing residue of the products of primary decomposition is immediately attacked by oxygen. The hydrogen atom, on the other hand, diffuses to the walls and is most likely adsorbed there.

This hypothesis is easily tested, for it is only necessary to pretreat the surface of tube B with hydrogen atoms produced photochemically by the reaction $Hg\ 2\,^3P_1 + H_2$ and determine explosion pressures. The water-cooled lamp was used during these experiments. Table X gives one series of results. The walls of the tube were washed down with phosphoric acid after each experiment and the pressure of hydrogen amounted to about 0·05 mm.

* 'Z. phys. Chem.,' vol. 15. B. p. 569 (1932).

Table X.

Explosion pressure.	Remarks.
19·0	Dark.
16·6	10 min. exposure.
19·6	Dark.
17·8	10 min. exposure.
21·8	Dark.
18·4	10 min. exposure.
20·4	Dark.

There is quite a definite decrease in explosion pressure. Separate experiments showed that the clean up of hydrogen was about 0·004 mm. per 10 minutes, the length and diameter of B being 15 cm. and 2 cm. respectively.

It remains to account for the decay of the effect. This may simply be due to the hydrogen atoms diffusing into the liquid phosphoric acid. Hence the decay period will depend on the phosphoric acid to some extent. Hinshelwood and Clusius actually found that large variations were obtained depending on the previous history of the acid. If the tube is not coated with acid another explanation of the decay can be advanced.

It has been shown by M. C. Johnson* that hydrogen atoms may remain on silica surfaces for long periods of time—much longer than the decay of the above effect. Recombination of the atomic hydrogen would therefore not account for the phenomenon. What would seem more likely is the attack of atomic hydrogen by impact of molecular oxygen on the surface.

Hydrogen saturated with mercury vapour was therefore admitted to a clean silica tube and part of it cleaned up by exposing the tube to the water-cooled lamp. Oxygen was then admitted and the pressures measured at suitable intervals. In Table XI it can be seen that the oxygen slowly attacks the

Table XI.

p_{H_2} initial	0·0735 mm.	0·0660 mm.	0·0465 mm.
p_{H_2} after clean up	0·0695 mm.	0·0625 mm.	0·0445 mm.
$p_{H_2+O_2}$	0·0910 mm.	0·0865 mm.	0·0800 mm.
$p_{H_2+O_2}$	After 8·5 minutes	After 9 minutes	After 10 minutes
	0·0905 mm.	0·0855 mm.	0·0780 mm.
$p_{H_2+O_2}$	After 18·5 minutes	After 19 minutes	After 20·5 minutes
	0·0900 mm.	0·0845 mm.	0·0780 mm.
$p_{H_2+O_2}$	—	After 29 minutes	—
		0·0845 mm.	

* 'Proc. Roy. Soc.,' A, vol. 123, p. 603 (1929); *ibid.*, A, vol. 128, p. 447 (1930); 'Proc. Phys. Soc.,' vol. 42, p. 490 (1930).

adsorbed hydrogen, since the total pressure of hydrogen + oxygen falls to a steady value after about 10–20 minutes. A liquid air trap was connected to the apparatus when the oxygen was admitted.

Langmuir* observed a similar disappearance of oxygen when it was admitted to a bulb in which hydrogen atoms had been produced by thermal dissociation on a hot tungsten filament.

In their experiments Hinshelwood and Clusius considered that light in the region 250–280 $\mu\mu$ (transmitted by a chlorine-bromine filter) was responsible, so that the initial stage of the reaction must have consisted in the photo-sensitised decomposition of phosphine due to the presence of some mercury vapour. The effect is not, however, dependent on whether the phosphine molecule is directly or indirectly dissociated so that illumination of the mixture by the unfiltered light from the hot arc would produce the same result.

Discussion of Mechanism of the Decomposition and Oxidation.

From these experiments the following mechanism can be proposed for the reaction. The phosphine molecule is dissociated, in the first place, by collision with excited mercury atoms into atomic hydrogen and a residue which is probably PH_2. The products of the dissociation diffuse to the walls of the tube, where they may recombine as is shown by the fact that as the surface/volume ratio of the tube is increased there is a decrease in the rate of decomposition. Recombination is extremely improbable in the gas phase as the concentration of the products of dissociation is small, and since the reaction is accompanied by the evolution of about 100 k. cal. per mole of PH_3 formed, a ternary collision would be necessary to effect stabilisation of the molecule. That recombination can occur between the phosphorus residue and hydrogen atoms is evident from the retardation of the reaction by atomic hydrogen. Formation of PH_3 from red phosphorus or phosphorus vapour and atomic hydrogen could not be detected in this investigation so that this provides further evidence that the atomic hydrogen unites with an intermediate product of the reaction.

If oxygen is added two effects are produced. First, the oxygen attacks the products of dissociation, thus preventing their recombination and therefore accelerating the rate of decomposition; second, the oxide molecule so formed (probably a phosphorus oxide and not H_2O, H_2O_2 or HO) initiates a stable chain reaction between the remaining phosphine and oxygen as is shown by the acceleration of this reaction by argon.

* 'J. Amer. Chem. Soc.,' vol. 34, p. 1310 (1912).

The inhibitory influence of molecular hydrogen is likewise due to two effects: (*a*) reduction of concentration of excited mercury atoms by deactivation, (*b*) reaction between atomic hydrogen and products of dissociation at the walls.

The production of molecular hydrogen during the decomposition is due to combination of atomic hydrogen probably at the walls. The PH_2 or PH radicles also may react at the walls,

$$PH_2 + PH_2 = P_2 + (2)H_2,$$

the P_2 molecules then polymerising to red phosphorus. P_2H_4 might have been formed just at N_2H_4 is produced under suitable conditions in the photodissociation of ammonia.* In view of the fact that the hydrogen pressure developed during the decomposition was almost equal to that predicted from the equation $4PH_3 = P_4 + 6H_2$, any formation of P_2H_4 must have been inappreciable. That P_2 molecules do polymerise on striking a glass surface was proved in an experiment carried out in connection with another investigation. In this, a beam of P_2 molecules obtained by passing P_4 molecules through a fine silica jet at 800° C. was directed towards glass targets cooled to various temperatures down to −80° C. After a suitable interval had elapsed a circular spot of red phosphorus had collected on the target.

The importance of surface effects was again emphasised in extending observations on the discovery of Hinshelwood and Clusius that illumination of PH_3-O_2 mixtures with a mercury arc resulted in a decreased explosion pressure. From the experimental evidence presented above, the dominant influence of hydrogen atoms is demonstrated. It is not at all clear how reaction chains are more efficiently reflected from a surface which is covered with hydrogen atoms. On p. 392 it was recorded that 0·004 mm. of hydrogen occupying about 300 c.c. or 10^{17} atoms adsorbed on 100 cm.^{2} of silica tube sufficed to produce the effect. A saturated layer of H atoms on 100 cm.^{2} amounts to about 10^{17} atoms.†

The author wishes to express his indebtedness to Dr. E. B. Ludlam for his constant advice and encouragement, to the Carnegie Trustees for a scholarship, to Imperial Chemical Industries, Ltd., and the Trustees of the Moray Research Fund of Edinburgh University for grants towards the cost of the apparatus.

* Gedye, ' J. Chem. Soc.,' p. 1158 (1932).

† Johnson, ' Trans. Faraday Soc.,' vol. 28, p. 161 (1932).

Summary.

The mercury photosensitised decomposition of phosphine has been investigated in some detail and the influence of the pressure of PH_3, H_2, O_2 and argon investigated in order to construct a mechanism for the reaction. The kinetics of this reaction are compared with those of ammonia. The ammonia results are recalculated on the basis of a new mechanism and compared with the direct photochemical reaction.

The lowering of the explosion limit of PH_3–O_2 mixtures by illumination with a mercury arc is shown to be due to a surface effect. The phenomenon can be reproduced by pretreatment of the walls with atomic hydrogen. A mechanism for the effect is suggested.

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The Diffusion Coefficients of Bromine-Hydrogen, Bromine-Nitrogen, Bromine-Oxygen, and Bromine-Carbon Dioxide.

By John E. Mackenzie, D.Sc., and
Harry W. Melville, Ph.D.

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By John E. Mackenzie, D.Sc., and Harry W. Melville, Ph.D. (Chemistry Department, University of Edinburgh).

(MS. received June 23, 1932. Read July 4, 1932.)

Introduction.

The early experiments on gaseous diffusion carried out by Joseph Priestley,* by John Dalton,† and by Berthollet ‡ led to the conclusion that a lighter gas diffuses more rapidly than a heavier one. Faraday § concluded from his experiments that "the actual relative mobilities of the gases are inversely as their specific gravities." Graham's classical work ‖ established quantitative relationships, of which perhaps the most important was: "The diffusion or spontaneous intermixture of two gases in contact is effected by an interchange in position of indefinitely minute volumes of the gases, which volumes are not necessarily of equal magnitude, being, in the case of each gas, inversely proportional to the square root of the density of that gas."

Measurements of diffusion as thus defined, that is diffusion of two gases in contact—without any septum between them—appear to be comparatively few. Graham's experiments in 1863 (*vide ante*) led to the more accurate work of Loschmidt,¶ which may be briefly described as follows: A glass tube was divided into two equal parts and these joined together by glass plates and a movable steel plate so arranged (*a*) that the circular holes cut in the glass plates and steel plate coincided with the bore of each half-tube, thus allowing uninterrupted passage of gas from one end to the other end of the tube; or (*b*) by pushing in the steel plate the upper half was completely cut off from the lower half of the tube. With the steel plate in position (*b*) each half was filled with a gas, the heavier gas being generally put in the lower and the lighter gas in the upper half of the vertical tube.

* *Experiments and Observations on different Kinds of Air*, 1777, iii, 301.

† *Phil. Mag.*, 1806, xxiv, 8.

‡ *Mém. d'Arcueil*, 1809, ii, 463.

§ *Quart. Journal of Sci.*, 1817, iii, 354 ; 1819, vii, 106.

‖ *Ibid.*, 1829, ii, 74 ; *Phil. Mag.*, 1833, ii, 175, 269, 351 ; *Brit. Assoc. Report*, 1845, 28 ; *Phil. Trans.*, 1846, iv, 573 ; 1849, ii, 349 ; 1863, 153, 385.

¶ *Wien. Sitz.*, 1870, lxi, 367 ; lxii, 468.

The steel plate was then moved to position (*a*), when diffusion commenced, and after a definite interval of time, say an hour, the steel plate was again brought to position (*b*) and the gas mixture in each half of the tube analysed. In this manner Loschmidt obtained data from which were calculated the diffusion coefficients of CO_2 : Air ; $CO_2 : H_2$; $H_2 : O_2$; $CO_2 : O_2$; $CO_2 : CO$; $CO_2 : CH_4$; $CO_2 : N_2O$; $SO_2 : H_2$; $CO : O_2$; $CO : H_2$.

Stefan * advanced the theoretical treatment of the subject, using the experimental results obtained by Loschmidt (*vide ante*), and his collaborators Wretschko † and Benigar,‡ and also calculated the diffusion coefficients of $(C_2H_5)_2O$: air and CS_2 : air from the rate of evaporation of these liquids contained in glass tubes of 2 to 6 mm. diameter. Winkelmann § extended this method to other vapours and gases, and later Stefan || summarised the results thus obtained.

Schmidt,¶ Jackmann,** Deutsch,†† and Lonius ‡‡ used a similar method, but replaced the glass tube by a steel tube provided with a steel stopcock, with opening of same bore as that of the tube, and in a second apparatus an additional stopcock divided the top half of the tube into an upper and a lower quarter. The data obtained from experiments with the second apparatus showed that the diffusion constant varied slightly with change in the relative concentration of the two gases.

The method described below presents an attempt to develop a method of measuring diffusion coefficients of vapours into gases. It allows of continuous observation of the process of diffusion and the making of a large number of measurements in one experiment. For this purpose the vapour of bromine is admirably adapted and its diffusion into a colourless gas is readily followed visually. Balard §§ in describing the newly discovered element said: "Il se volatilise aisément, et cette grande volatilité contraste beaucoup avec sa pesanteur spécifique: il suffit de mettre une goutte de brôme dans un vase quelconque, pour que sa capacité soit à l'instant remplie par une vapeur rutilante très foncée. . . ."

* *Wien. Sitz.*, 1871, lxiii, 63 ; 1872, lxv, 323 ; 1873, lxviii, 385.
† *Ibid.*, 1870, lxii, 575.
‡ *Ibid.*, 1870, lxii, 687.
§ *Ann. d. Physik*, 1884, xxiii, 203 ; 1885, xxvi, 105.
|| *Ibid.*, 1890, xli, 725.
¶ *Ann. d. Physik*, 1904, xiv, 801.
** *Inaug. Diss. Halle*, 1906.
†† *Ibid.*, 1907.
‡‡ *Ann. d. Physik*, 1909, xxix, 664.
§§ *Ann. Chim. Phys.*, 1826, (2), 32, 337.

Experimental.

The apparatus (fig. 1) is a glass tube A, 1500 mm. in length and 29·8 mm. in diameter (internal). A tap funnel B is sealed to the lower end of A and the upper end is closed by a rubber stopper C provided with a glass tap D. A is filled with hydrogen or other gas, and bromine is then poured into B. The barometric pressure and room temperature having been measured, bromine is run from B into A, so that the surface of the liquid bromine is about 25 mm. in diameter, the time is noted and tap D opened momentarily to equalise the pressure. A white filter-paper screen behind the tube showed up the reddish-brown vapour of bromine. At short intervals of time the height above the surface of the liquid bromine at which the colour of the bromine vapour just becomes perceptible is measured.

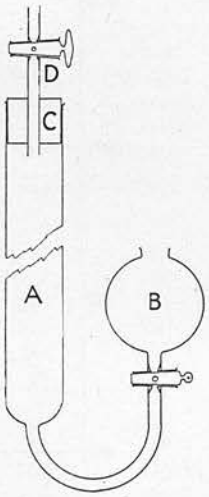

Fig. 1.

The observations were made in a room with a very large window having an uninterrupted northern exposure. Experiments made on different days and by different observers (having normal colour vision) gave closely concordant data, so that it may be concluded that slight variations in the brightness of the northern sky did not appreciably affect the readings of the heights of the bromine-vapour column. The hydrogen, nitrogen, oxygen, and carbon dioxide were supplied by the British Oxygen Company, and before introducing into the tube A were bubbled through concentrated sulphuric acid.

In this manner measurements were made with pairs of gases and bromine vapour, using two diffusion tubes side by side in order that relative as well as absolute measurements might be made. A large number of experiments were made, and the data given in Table I and plotted along with others, in fig. 2, are typical.

In order to calculate the absolute value of the diffusion coefficient (D), it is necessary to know the concentration of bromine vapour (n), which can just be seen in the apparatus used for these experiments. This concentration was measured as follows. A 12-litre flask with a neck of the same diameter as that of the diffusion tube was filled with hydrogen, and then bromine vapour was introduced until, after thorough mixing, it was just visible in the neck. The use of the flask instead of the diffusion tube rendered the adjustment of the bromine concentration much easier owing to the gradation of intensity of the colour of the bromine vapour from the middle to the neck

of the flask. In addition the use of a large flask permitted of a more accurate determination of the concentration of the bromine vapour. The flask was connected on one side to a gas wash-bottle containing sulphuric acid and

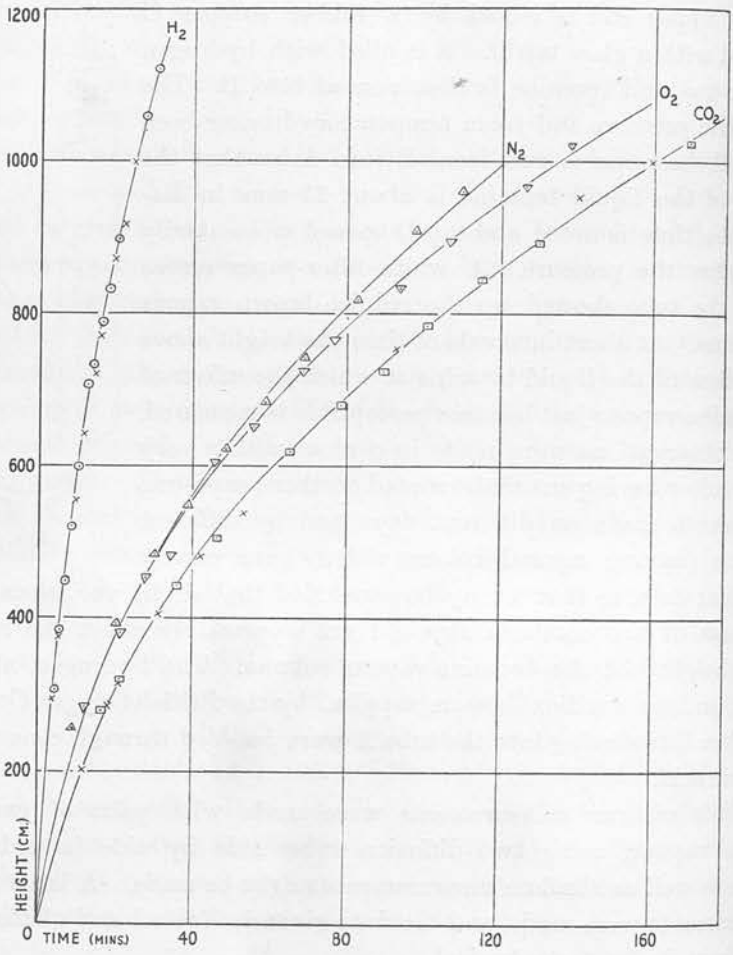

FIG. 2. × denotes readings made on 23.2.32 at 15° and 767 mm. for $Br_2 : H_2$, and on 2.24.32 at 15° and 764 mm. for $Br_2 : CO_2$.

on the other to two sets of Geissler bulbs in series containing potassium iodide solution and to a large aspirator. Air was then drawn through the apparatus until all the bromine had been transferred from the flask to the Geissler bulbs. The amount of iodine liberated was estimated by standard thiosulphate solution. Three estimations gave the following results: 2·66, 2·57, 2·79 grm. of Br_2 per 10^6 c.c., which is equivalent to a pressure of Br_2 of 0·275 mm.

TABLE I.

Bromine-Hydrogen.		Bromine-Nitrogen.		Bromine-Oxygen.		Bromine-Carbon Dioxide.	
Time. (min.).	Height at which Bromine Vapour is just visible. (mm.)	Time. (min.)	Height at which Bromine Vapour is just visible. (mm.)	Time. (min.)	Height at which Bromine Vapour is just visible. (mm.)	Time. (min.)	Height at which Bromine Vapour is just visible. (mm.)
0	..	0	..	0	..	0	..
4	306	8	254	11	285	17	280
5	386	20	389	21	385	22	320
6	446	30	479	28	455	32	375
8	518	39	544	35	485	44	485
10	601	49	619	45	605	55	565
13	709	59	679	56	655	66	620
14	736	71	739	68	725	79	675
17	791	83	814	77	765	90	720
19	836	98	909	93	835	101	780
22	906	110	959	106	905	115	845
27	1058	121	1024	119	955	130	890
31	1118	147	1089	124	965	143	925
36	1258	..	..	148	1025	170	1025
..	..	..	..	163	1065	..	..
..	..	..	..	182	1135	..	..
Pressure . 774 mm. Temp. . 286° K. Date . 18.2.32		Pressure . 772 mm. Temp. . 286° K. Date . 22.2.32		Pressure 766·5 mm. Temp. . 286° K. Date . 1.3.32		Pressure . 768 mm. Temp. . 286° K. Date . 25.2.32	

CALCULATION OF DIFFUSION COEFFICIENT.

The diffusion coefficient of a single gas may be defined by the general equation

$$\frac{dn}{dt} = D\left(\frac{d^2n}{dx^2} + \frac{d^2n}{dy^2} + \frac{d^2n}{dz^2}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n is the number of molecules per c.c., x, y, and z are co-ordinates of a given point in the gas, t being the time and D the diffusion coefficient. If, for simplicity, diffusion in a long cylindrical tube is considered, then equation (1) may be simplified to

$$\frac{dn}{dt} = D\frac{d^2n}{dx^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

x being measured along the axis of the tube, this equation being the expression of Fick's diffusion law. In order to integrate (2) the limiting

conditions must be known. If it is assumed that the concentration is kept constant at one end of the tube, i.e. $n = n_0$ for $x = 0$, then (2) becomes, on integration,*

$$n = n_0 e^{-x^2/2Dt}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Hence if n is measured at x after a given time interval t, D may be calculated from (3).

Before it is possible to calculate D from the above data an important correction must be applied. Since the tap at the top of the diffusion tube is kept shut, the pressure will gradually rise as the bromine evaporates. If $\bar{p}$ is the mean pressure of the bromine, x_0 the length, and A the area of cross-section of the diffusion tube,

$$\bar{p} A x_0 = A \int_0^{x_0} p dx$$

or

$$\bar{p} = \frac{1}{x_0} \int_0^{x_0} p dx = \frac{1}{x_0} \int_0^{x_0} p_0 e^{-x^2/2Dt} dx.$$

The integral is most conveniently evaluated graphically. Now $p = p_0 e^{-kx^2}$, and let $k = 1/2Dt$. Since p and p_0 are known, then the value of k for any value of x may be computed and therefore the curve of p against x plotted. This was done for three values of x, viz. 70, 87·5, and 110 cm., the area of the curves determined by a planimeter, and the mean value of the pressure of the bromine vapour obtained from the above equation.

The following results were obtained:

x . . .	70	87·5	110 cm.
p . . .	20·2	24·8	32·5 mm.

The values of t for $x = 70$, 87·5, and 110 cm. were obtained from fig. 2. Using equation (3), D was calculated for the pressure prevailing in the diffusion tube, and then by multiplication by the factor—total pressure/760—D_{760} was evaluated. The results of the calculation are shown in Table II.

D calc. may be obtained in various ways by using the different equations which have been advanced from time to time, and the values thus got are in fairly close agreement. In a recent comprehensive survey of diffusion coefficients, Arnold † concludes that the diffusion equation given by Jeans‡ agrees best with the experimental data. The diffusion coefficient is given by the equation

$$D = \frac{K}{\sigma_{12}^2} \sqrt{\frac{1}{M_1} + \frac{1}{M_2}}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

* *Cf.* Eucken, *Lehrbuch der chemischen Physik*, p. 522.

† *Industrial and Engineering Chem.*, 1930, xxii, 1091.

‡ *Dynamical Theory of Gases*, 4th ed., chap. xiii.

where K is a constant provided the temperature is a constant, σ_{12} the sum of the radii of the molecules, and M_1 and M_2 the molecular weights of the gases 1 and 2.

TABLE II.

Gas Mixture.	x (cm.).	t (min.).	p (mm.).	Total Press.	D cm.^{2} sec.$^{-1}$	D_{760}.	D calc.
Br_2/H_2	70·0	13·0	20·0	794·0	0·513	0·538	..
	87·5	20·0	25·0	799·0	0·521	0·550	0·598
	110·0	30·0	32·5	806·5	0·546	0·580	..
Br_2/N_2	70·0	61·0	20·0	792·0	0·110	0·115	..
	87·5	92·0	25·0	799·0	0·113	0·119	0·132
	110·0	146·0	32·5	806·0	0·113	0·120	..
Br_2/O_2	70·0	63·0	20·0	786·0	0·104	0·109	..
	87·5	101·0	25·0	791·0	0·103	0·108	0·133
	110·0	178·0	32·5	806·0	0·093	0·099	..
Br_2/CO_2	70·0	84·0	20·0	788·0	0·079	0·083	..
	87·5	126·0	25·0	793·0	0·083	0·087	0·107
	110·0	..	..	..	..	..	..

For $H_2 : O_2$ Arnold concludes from theoretical considerations that the most probable value of D_{12} is 0·70. Using this value, the constant K of equation (4) was determined by substituting the appropriate values for σ and M_1 and M_2, and found to be $7{\cdot}02 \times 10^{-16}$. In Table II, D calc. was got by using this *theoretical* value of K and the following values of σ—Br_2, $1{\cdot}71 \times 10^{-8}$ cm.; H_2, $1{\cdot}15 \times 10^{-8}$ cm.; N_2, $1{\cdot}55 \times 10^{-8}$ cm.; O_2, $1{\cdot}45 \times 10^{-8}$ cm.; CO_2, $1{\cdot}60 \times 10^{-8}$ cm.

It is to be noted that the observed diffusion coefficients are consistently lower than the calculated values. A similar difference between observed and calculated diffusion coefficients is found in the data given by Arnold * for mixtures of gases, and of vapours and hydrogen, but not of vapours with air or carbon dioxide.

With the one exception of $Br_2 : O_2$ at $t = 178$ min. (which may be due to experimental error), D_{760} increases with time of diffusion. Hence the diffusion coefficient is dependent to some slight extent on the composition of the vapour-gas mixture, as has been previously found to be the case with most gas mixtures (*see* p. 338). It is probable that the experimental values of D would approach closely to the calculated values if the diffusion were allowed to proceed further until an approximately equimolecular mixture was obtained.

* *Industrial and Engineering Chem.*, 1930, xxii, 1091.

SUMMARY.

A brief history of the measurement of diffusion of gases (excluding "effusion," "transpiration," and other processes from which data for the calculation of the diffusion coefficient may be obtained) is given.

A visual method of following the diffusion of a strongly coloured vapour (bromine) into colourless gases is described.

The diffusion coefficients calculated from the observed data are in good accordance with those obtained theoretically.

The authors desire to thank Miss Netta Macnaughton for valuable assistance in the experimental work.

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UPPER LIMIT IN EXPLOSIVE CHAIN REACTIONS

BY

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THE existence of an upper limiting pressure for explosion in thermal chain reactions has been explained in two ways. (1) The rate of branching of the chains, at the limit, is just sufficient to balance the rate of gas phase deactivation of the carriers; (2) a sudden change in the nature of the absorbed layer of gas on the walls of the reaction tube leads to the ejection of atoms or molecules into the gas capable of starting the chain. In two recent letters[1] to NATURE, the gas phase deactivation theory has been further extended to explain the occurrence of the upper limit. It may be of interest, therefore, to describe an experiment with phosphine-oxygen mixtures in which it can be shown that in the region above the upper limit there is a gradual decrease in the length of the reaction chains as the pressure is increased.

In order to initiate the chain, dissociation of the phosphine molecule was effected by collision with an optically excited ($2\,^3P_1$) mercury atom[2]. The pressure of the phosphine was maintained at a constant value (0·130 mm. mercury) and a series of experiments was made at different oxygen pressures with the mercury lamp burning at a constant intensity. As can be observed from Fig. 1, the rate of reaction increases at first, reaches a maximum and then decreases; and the pressure of oxygen at the maximum is of the same order as that where the curves representing the upper and the lower limit coincide[3]. The chain length consequently increases in the region below the lower limit, but above the upper limit it apparently decreases as the pressure of gas rises.

It might be argued that this decrease in chain length is due to deactivation of the mercury atoms by oxygen as the oxygen pressure is increased,

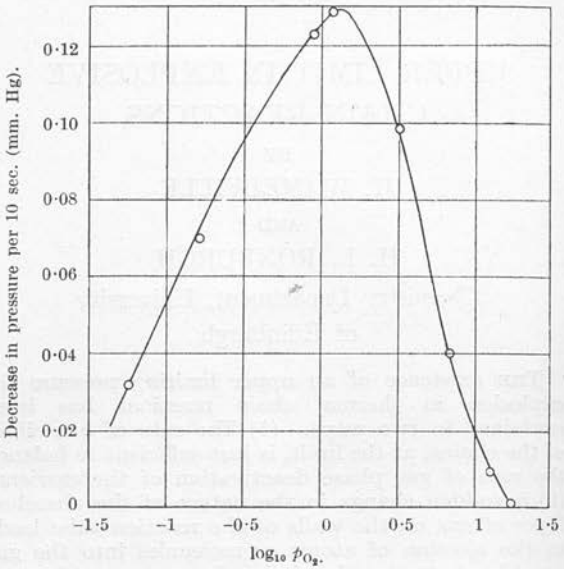

FIG. 1.

Taking this factor into account, the rate of oxidation of phosphine is then given by

$$R = -\frac{d[PH_3]}{dt} = \frac{K_1 k_1 [PH_3]}{k_1[PH_3] + k_2[O_2] + 1/\tau} \cdot K_2[PH_3] f([O_2]),$$

the first term representing the rate of starting and the second the chain length; k_1 and k_2 are velocity coefficients and τ the mean life of the excited mercury atom. If $f([O_2]) = [O_2]$, as is probably the case below the lower limit, R would increase with $[O_2]$ and tend to a maximum steady value when $[O_2] >> [PH_3]$. The fact that R decreases shows that $f([O_2])$ is of the form $1/[O_2]^n$ and hence the chain length must decrease as $[O_2]$ increases. From the results, it may be readily shown by plotting $1/R$ against $[O_2]^2$ that n approaches unity. The oxygen molecule is thus an inhibitor for the reaction in this region by virtue of its deactivating influence on the chain carriers in the gas phase. As the upper limit is approached, such deactivation diminishes until the rate of branching effects a balance between the two, and explosion occurs.

[1] Ubbelohde, March 4, p. 328; Hinshelwood and Grant, March 11, p. 361.
[2] Melville, *Proc. Roy. Soc.*, A, **138**, 374; 1932.
[3] Dalton, *ibid.*, A, **128**, 263; 1930.

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147. *The Thermal Decomposition of Phosphine by Tungsten and Molybdenum.*

By H. W. Melville and H. L. Roxburgh.

Recent investigations on the kinetics of thermal chain reactions have emphasised the fact that surfaces are responsible not only for the termination of chains but also for their initiation (cf. Hinshelwood, *Trans. Faraday Soc.*, 1932, **28**, 184). The latter effect extends to the explosive reaction and to the stable chain reaction, which occurs, in some cases, in the region outside the explosion limits. Whilst the kinetics of explosions have been satisfactorily worked out, in a general manner, notably by Hinshelwood and by Semenoff, the investigation of possible stable chain processes is more likely to lead to a better understanding of the mechanism, as a wider variety of conditions for reaction can be studied and also more easily controlled.

A chain reaction consists essentially of three distinct phenomena, *viz.*, (*a*) initiation, (*b*) propagation, (*c*) termination of the chain. In order to investigate the kinetics of a reaction in detail, some means are required to separate these processes. Since the start of chains depends upon the introduction of reactive molecules or atoms into the gas mixture, a variety of ways exists whereby initiation may be induced. It has been shown (Melville and Ludlam, *Proc. Roy. Soc.*, 1932, *A*, **135**, 315) that in the oxidation of phosphorus a tungsten, molybdenum, or glass filament is capable of initiating a stable chain reaction below the lower limit. This reaction has many of the chain characteristics of the explosive reaction at the lower limit (Semenoff, *Z. Physik*, 1927, **46**, 109). By the use of a hot filament, then, a method is available in certain circumstances whereby the initiation of chains may be accurately controlled, provided that the mixture be in a condition to propagate chains once they have been started.

The kinetics of the oxidation of phosphine and of phosphorus are very similar. Further it has been shown (Melville, *Proc. Roy. Soc.*, 1932, *A*, **138**, 374; 1933, *A*, **139**, 541) that a stable chain reaction may be started by excited mercury atoms or by the direct photochemical decomposition of the phosphine molecule. The photochemical experiments have also indicated a chain length very nearly equal to that calculated on the assumption that

FIG. 1.

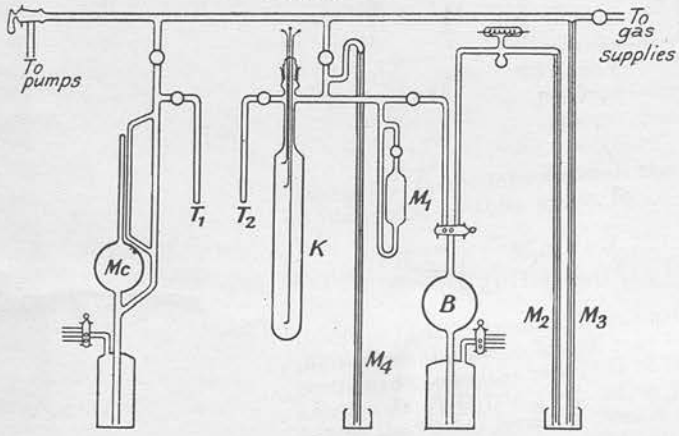
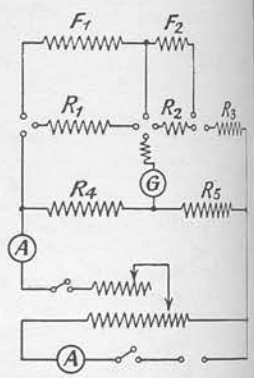


FIG. 2.



reaction occurs at every collision between chain carriers and reactant molecules. Phosphine–oxygen mixtures below the lower explosion limit are therefore capable of propagating chains with suitable primary stimulation.

It was consequently anticipated that the oxidation of phosphine, like that of phosphorus, might be induced by hot filaments. Before such an investigation could be carried out, it was necessary to study the kinetics of the decomposition of phosphine on tungsten and molybdenum filaments. The present paper is concerned with this aspect of the problem, and the oxidation will be dealt with in another communication.

EXPERIMENTAL.

Preparation of Gases.—PH_3 was prepared by dropping KOH aq. on PH_4I, passing the PH_3 evolved over NaOH, $CaCl_2$, and P_2O_5, and collecting in a liquid-air trap. The PH_3 was then subjected to fractional distillation. The H, O, and A were taken from cylinders and purified by the usual methods, all gases being dried with P_2O_5.

Apparatus.—The essential parts of the apparatus are shown diagrammatically in Fig. 1. The reaction tube (*K*) was 3 cm. wide and about 20 cm. long. This was surrounded by a water-bath maintained at a const. temp. (usually about 20°). *K* was exhausted by a Hg condensation pump backed by a Hyvac oil pump. In addition to the gas reservoirs and pipettes, suitable side tubes cooled in liquid air were connected to the apparatus in order to facilitate the analysis of gas mixtures containing PH_3. A small Töpler pump (*B*) was used for transferring gas in *K* to a tube containing a Pt wire for analysing the H–O mixtures obtained in the oxidation expts.

Several types of pressure gauge were employed. For the lowest pressures, a McLeod gauge (M_2) was most convenient, but for somewhat higher pressures a glass spring manometer was used. Later expts. were made with an oil manometer (M_1). The right (exhausted) limb was of much wider tubing (2·5 cm. diam.) than the left limb (0·4 cm.), so the movement of the oil in the left limb for a given pressure change was nearly double that in a manometer with limbs of equal bore. Apiezon oil " B " (Shell-Mex and B.P.) of v.p. $< 10^{-7}$ mm. Hg proved to be suitable, as it did not appreciably dissolve the gases which were used in these expts. The oil was thoroughly degassed before use by warming in a vac. A sensitivity of 0·001 mm. was easily reached by using a microscope to read the position of the oil. M_2, M_3, and M_4 were capillary Hg manometers. Apiezon grease " L " was used as a tap lubricant.

Determination of Filament Temperature.—In order to eliminate, as far as possible, end losses, the filament was constructed in an unusual manner. Preliminary expts. had shown that the rate of decomp. of the PH_3 was conveniently measurable at temps. below 600°, so it was not possible to read the temperature of the centre portion of the filament by a micropyrometer and correct for end losses by calculation (Langmuir, MacLane, and Blodgett, *Physical Rev.*, 1930, 35, 478).

The principle of this new method is as follows. Two filaments, one 3—4 times longer than the other, are set up in the reaction tube and run under identical conditions. The reaction velocity due to each filament is determined as well as the " hot and cold " resistance of the two filaments. The rate of reaction on the filament minus the rate on the small filament is therefore the rate due to a central portion of the large filament which is at an approx. const. temp. throughout its length. Similarly, the difference in resistances of the two filaments gives the resistance of this central portion, and from the resistance–temp. relation of the metal, the mean temp. of the central portion can be accurately calculated. To ensure that the filaments did run under precisely identical conditions, each formed the arm of a Wheatstone bridge, in which circumstances small losses in the connecting leads were simultaneously balanced out.

The filament was spot-welded to 1 mm. Ni leads, " copper clad " wire being used to make the metal-glass seals. The electrical connexions are shown in Fig. 2. F_1 and F_2 denote the large and the small filament respectively, whilst R_1 and R_2 are variable resistances whereby F_1 or F_2 can be balanced out; R_3 is a fixed resistance. R_1, R_2, and R_3 were all made of constantan wire of such a diameter as to carry the bridge current without appreciably changing in resistance. R_4 and R_5 are much higher resistances (*ca.* 1000 ohms).

Before setting up the bridge, it was necessary to find how long the small filament should be in order to eliminate end losses. The choice of dimensions was facilitated by the fact that when PH_3 is decomposed on the W or the Mo filament a deposit of red P is formed on the walls of the tube containing the filament. The density of distribution of this deposit, when the decomp. was carried out at low press., indicated approx. the effective length of the filament. For a 12-cm. filament, this length was found to be *ca.* 9 cm. at the temps. used in these expts. The small filament was therefore made 3 cm. long.

With F_1 and F_2 in circuit, suitable temp. and press. ranges were found, and the bridge was balanced by the adjustment of R_5. A run was then made, and the velocity calculated according to the methods described below. With the same press. of PH_3, another run was carried out, R_1 being substituted for F_1. The rate due to F_2 was thus obtained, and by subtraction the rate due to the central portion of F_1. R_1, R_2, R_3, R_4, and R_5 were all known, so the resistance of F_1 and of F_2 could easily be calculated.

If for any reason the temp. of the filament was changed, the above balancing was repeated. In the comparatively small temp. range which could be conveniently used, it was unnecessary to find the reaction velocity due to each filament at the several temps. used. A small correction —4%—was applied to the rate of reaction with both filaments in circuit in order to reduce this rate to that due to the central portion of the large filament. The bridge currents, with 0·1 mm. diam. wires, ranged from 0·3 to 1·5 amp. On each occasion in which a new filament was put into use it was subjected to a thorough out-gassing for several hr. under 10^{-5} mm. The resistance–temp. curves for each specimen of wire were separately determined.

Although W and Mo were used entirely in these expts., one or two runs were made with Ni and with a Ni–Fe alloy. The temp. to which these required to be heated was approx. the same as that for W and Mo, but they did not survive more than one or two expts. involving the decomp. of about 5 mm. PH_3 in a vol. of 200 c.c. The P appeared to attack the metal, rendering it very brittle and finally causing its complete disintegration, presumably owing to formation of a phosphide. Mo and W seemed to withstand the reaction for an indefinite period without undergoing any marked change in catalytic activity.

Molybdenum Filament.

Products of Reaction.—There is a press. increase during the decomp. which must be due to H, but the question arises as to whether all of the H is liberated into the gas phase. Experimental data given below support the view that the decomp. can be represented by the equation $4PH_3 = P_4(red) + 6H_2$, no appreciable proportion of P_2H_4 or any of the solid hydrides of P being formed.

What is more important, from the point of view of possible chain-initiator molecules, is the mechanism of the formation of the P. Although a red deposit appears on the walls of the reaction tube, P vapour may also be produced. There are, therefore, two possible end states in which P might occur: (1) a mixture of red P, white P, and P vapour; (2) red P entirely. Another possibility is the intermediate formation of P_4 or of white P, since normal P_4 molecules might evaporate off the filament, in the first instance, collide with the walls, and eventually return to the filament, whereby they are altered in some manner so that on colliding with the walls again red P is formed. The formation of red P from P vapour (P_4 mols.) has been repeatedly observed in a tube containing a W or Mo filament sufficiently hot to decompose PH_3.

To decide the matter, the following expt. was made, which was typical of many. 0·92 Mm. of PH_3 was admitted to the reaction tube, which was surrounded by a CO_2–Et_2O bath at −. The filament was heated until there was no further press. change; the press. increase was 0 mm., thus confirming the equation given above. The H was pumped off and the bath withdrawn to allow any white P to evaporate. 0·63 Mm. of O was added, but no glow could be observed nor was there any observable press. change. The absence of glow indicated that the press. of P_4 was less than 2×10^{-3} mm., which is the p_{P_4} at the lower explosion limit with 0·6 mm. of O in a 2 cm. tube. No appreciable amount of P vapour was thus formed. Had the P evaporated from the filament as normal P_4 mols., these would have condensed on the cool glass surface and re-evaporated when the reaction tube was warmed to room temp. This expt. also provides evidence that there is no intermediate formation of white P, or of P vapour. The P must therefore leave the filament in such a form that it condenses on the surface, is adsorbed, and ultimately forms red P. It has been shown (Melville, *Proc. Roy. Soc.*, 1932, *A*, **138**, 394) that P_2 mols. polymerise to red P on hitting a glass surface, and therefore it is probable that the P leaves the filament as P_2 mols.

Another confirmatory experiment was made. 6 Mm. of PH_3, occupying 200 c.c., gave a film of red P which just exhibited interference colours. The film was 10 cm. long and the diameter of the tube 2 cm., so that it would require at least 3×10^{-3} g. of red P to form such a film, whereas 200 c.c. of PH_3 at 6 mm. would yield $2{\cdot}4 \times 10^{-3}$ g. of P on being decomposed.

A curious effect was noticed during this work. Although the film of red P was usually of uniform thickness, in some instances, patches of the reaction tube remained only slightly covered, whilst in other parts the deposit was dense. It would appear that the walls exert a definite activity towards the deposition of red P. It is of interest, therefore, that, not only is the combination of atoms on a wall dependent on its nature, but, in this case, the polymerisation of mols. is likewise affected. No expts. have been carried out with walls of different material, but the reaction tubes were cleaned with Br aq. to remove red P and were subsequently washed out with H_2O and dried.

As these expts. are preliminary to the study of the oxidation at press. below the lower explosion limit, the press. of PH_3 used ranged from a few mm. down to the lowest press. which could be measured on the McLeod gauge. The general procedure (at higher press.) was to admit PH_3, note its press., switch on the filament current, and take press. readings at convenient time intervals. Upon heating the filament, however, there is a small press. increase due to heating of the gas. A correction has to be applied to the observed press. in order to find the true value at the temp. of the walls of the reaction tube; this was measured by filling the reaction tube with O and finding the press. increase on heating the filament to the temp. at which it was to be subsequently employed. This procedure was repeated for different press. O has nearly the same thermal conductivity as PH_3 and does not react with filament at the temp. used for the decomp. of PH_3. A similar series of expts. was made with H. As the correction for O was only double that for H, a linear relation was considered to be sufficiently accurate when calculating the correction for mixtures of the two. The appropriate correction could then be applied for the PH_3–H mixture as the H accumulates during the reaction. For a 1 : 1 mixture, therefore, the correction factor is the mean of that for PH_3 and for H alone.

A typical series of press.–time observations at a number of different initial PH_3 press. is given in Table I, $t_{\frac{1}{2}}$ being the time of half-decomp. All press. are in mm. Hg, and times (

min.; col. 2 ($p_{PH_3+H_2}$) is the actual obs. press., Δp is the press. increase corrected for the small heating effect.

TABLE I.

Length of Mo filament, 14·9 cm.; diam. of filament, 0·01 cm.; temp. of filament, 464°; vol. of reaction tube, 90 c.c.; temp. of reaction tube, 20°.

Expt. 59.

t.	$p_{PH_3+H_2}$.	Δp.	$\Delta p/t$.
0	0·67	0	—
0·5	0·74	0·04	0·08
1·0	0·78	0·07	0·07
1·5	0·81	0·10	0·07
2·0	0·84	0·15	0·075
2·5	0·86	0·17	0·068
3·0	0·90	0·21	0·070
3·5	0·92	0·23	0·066
4·0	0·93	0·24	0·060
4·5	0·94	0·25	0·056
5·0	0·95	0·26	0·052
5·5	0·96	0·27	0·049
	Δp_∞	0·34	
	$t_{\frac{1}{2}} = 2·4$ min.		

Expt. 60.

t.	$p_{PH_3+H_2}$.	Δp.	$\Delta p/t$.
0	1·16	0	—
0·5	1·25	0·04	0·08
1·0	1·30	0·09	0·09
1·5	1·34	0·13	0·087
2·0	1·38	0·17	0·085
2·5	1·41	0·21	0·084
3·0	1·44	0·24	0·080
3·5	1·47	0·27	0·077
4·0	1·50	0·30	0·075
5·0	1·56	0·37	0·074
6·0	1·62	0·43	0·071
8·0	1·68	0·49	0·061
10·0	1·73	0·54	0·054
12·0	1·75	0·56	0·047
		Δp_∞ 0·58	
		$t_{\frac{1}{2}} = 3·6$ min.	

Expt. 61.

t.	$p_{PH_3+H_2}$.	Δp.	$\Delta p/t$.
0	2·01	0	—
0·5	2·12	0·02	0·040
1·0	2·17	0·07	0·070
1·5	2·22	0·13	0·087
2·0	2·27	0·18	0·090
3·0	2·34	0·25	0·081
4·0	2·42	0·34	0·085
5·0	2·50	0·42	0·084
6·0	2·57	0·50	0·081
7·0	2·65	0·58	0·082
8·0	2·71	0·64	0·080
10·0	2·79	0·73	0·073
12·0	2·85	0·79	0·066
14·0	2·90	0·84	0·060
		Δp_∞ 1·00	
		$t_{\frac{1}{2}} = 6·0$ min.	

Expt. 62.

t.	$p_{PH_3+H_2}$.	Δp.	$\Delta p/t$.
0	2·74	0	—
0·5	2·86	0·01	—
1·0	2·93	0·07	0·07
1·5	2·95	0·10	0·067
2·0	3·01	0·16	0·080
3·0	3·11	0·27	0·090
4·0	3·20	0·36	0·090
5·0	3·31	0·48	0·090
6·0	3·38	0·55	0·091
8·0	3·52	0·69	0·086
10·0	3·68	0·85	0·085
12·0	3·79	0·97	0·081
14·0	3·88	1·06	0·075
16·0	3·97	1·15	0·072
18·0	4·00	1·19	0·067
20·0	4·03	1·22	0·061
		Δp_∞ 1·37	
		$t_{\frac{1}{2}} = 8·0$ min.	

Expt. 63.

t.	$p_{PH_3+PH_3}$.	Δp.	$\Delta p/t$.
0	3·58	0	—
0·5	3·79	0·06	0·120
1·0	3·86	0·13	0·130
1·5	3·89	0·17	0·113
2·0	3·94	0·22	0·110
3·0	4·01	0·29	0·097
4·0	4·14	0·43	0·107
6·0	4·33	0·63	0·105
8·0	4·48	0·78	0·099
10·0	4·62	0·93	0·093
12·0	4·78	1·10	0·092
14·0	4·88	1·20	0·086
16·0	5·00	1·33	0·083
19·0	5·08	1·41	0·074
		Δp_∞ 1·79	
		$t_{\frac{1}{2}} = 9·5$ min.	

The first characteristic of these expts. is that the time required for half-decomp. increases with the press. of the PH_3. Similarly, the initial rate of reaction is maintained and does not decrease until a large fraction of the PH_3 is decomposed. Further, the initial rate only increases 50% for a press. increase from 0·67 to 3·58 mm. PH_3.

The effect of H was next investigated to find whether it might modify the course of the decomp. as it accumulates in the system: no influence could be measured, the half-life being independent of H press., as is shown by the following two series of results:

Expt.	24	25	26	28	29
p_{PH_3}	1·98	1·92	1·84	2·01	1·84
p_{H_2}	—	0·92	1·79	—	2·90
$t_{\frac{1}{2}}$	1·6	1·9	1·8	1·6	1·5

It may be concluded, therefore, that at pressures of the order of a few mm. of Hg, the course of the decomp. conforms nearly to a reaction of zero order.

Low-pressure Experiments.—The deviations of the above results from a zero-order reaction suggested that at lower press., adsorption of PH_3 might be so much less marked that the reaction would become unimol. The expts. were made with the McLeod gauge as manometer, and consequently the procedure had to be slightly modified. PH_3 to the required press. was passed into the reaction system and the filament switched on for a given time, after which the total press. was determined. This was repeated until practically all the PH_3 was decomposed. Conditions were arranged so that the time required to heat the filament to its working temp. was about 1% of the time of reaction. The vol. of the McLeod gauge and connexions was determined,

so the obs. reaction velocity could be reduced to the value obtaining in the reaction tube u in the high-press. expts.

Table II gives a typical series of runs using the same filament temp. as in Table I; k is unimol. coeff., $1/t \,.\, \log_{10} a/(a - x)$, where a is the initial press. of PH_3 and x that of decomp PH_3. The vol. of the apparatus was 390 c.c.

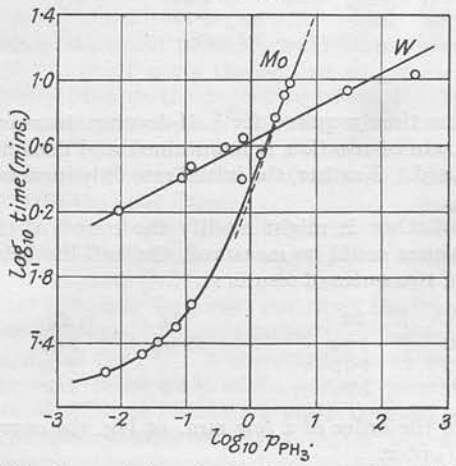
TABLE II.

t.	p_{PH+H_2}.	Δp.	k.	$\Delta p/t$.	t.	$p_{PH_3+H_2}$.	Δp.	k.	$\Delta p/t$.
		Expt. 67.					Expt. 68.		
0	0·1240	0	—	—	0	0·0695	0	—	—
1	0·1450	0·0210	0·178	0·021	1	0·0845	0·0150	0·246	0·015
2	0·1585	0·0345	0·176	0·0173	2	0·0925	0·0230	0·236	0·011
3	0·1690	0·0450	0·180	0·0150	3	0·0970	0·0275	0·227	0·009
4	0·1755	0·0515	0·193	0·0129	4	0·0985	0·0290	0·196	0·007
6	0·1825	0·0585	0·209	0·0098	6	0·1000	0·0305	0·133	0·005
8	0·1835	0·0595	—	0·0074	8	0·1115	0·0320	0·146	0·004
		Δp_∞ 0·0620					Δp_∞ 0·0347		
		$t_{\frac{1}{2}}$ 1·8 min.; $t'_{\frac{1}{2}}$ 0·42 min.*					$t_{\frac{1}{2}}$ 1·35 min.; $t'_{\frac{1}{2}}$ 0·313 min.		
		Expt. 69.					Expt. 70.		
0	0·0385	—	—	—	0	0·0190	—	—	—
1	0·0490	0·0105	0·342	0·0105	1	0·0235	0·0445	0·278	0·044
2	0·0520	0·0135	0·263	0·0067	2	0·0270	0·0080	0·217	0·004
3	0·0550	0·0165	0·282	0·0055	3	0·0275	0·0085	0·328	0·002
4	0·0565	0·0180	0·297	0·0045	4	0·0277	0·0087	0·259	0·002
		$t_{\frac{1}{2}}$ 1·08 min.; $t'_{\frac{1}{2}}$ 0·251 min.					Δp_∞ 0·0095		
							$t_{\frac{1}{2}}$ 0·95 min.; $t'_{\frac{1}{2}}$ 0·220 min.		
							Expt. 71.		
0	0·0060	0	—	—	3	0·0087	0·0027	0·33	0·000
1	0·0080	0·0020	0·176	0·0020	4	0·0087	0·0027	—	0·000
2	0·0085	0·0025	0·38	0·0013			$t_{\frac{1}{2}}$ 0·70 min.; $t'_{\frac{1}{2}}$ 0·162 min.		

* $t'_{\frac{1}{2}}$ is the value $t_{\frac{1}{2}}$ would have in a reaction vessel of the vol. used in the high-pressure expt.

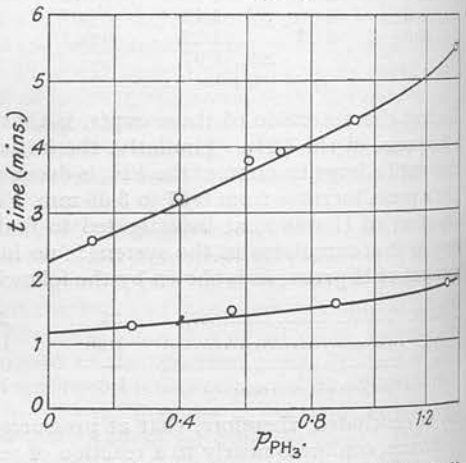
Even at quite low press., the time required for half-decomp. is slightly dependent on pres but the approx. constancy of the values in col. 4 of Table II indicates that the reaction is ve nearly unimol. The value of $\Delta p/t$ drifts considerably, as is to be expected.

FIG. 3.



The $\log_{10}$ of time for half decomposition (Mo) *and for quarter decomposition* (W) *of* PH_3 *plotted against* $\log_{10} p_{PH_3}$. *The broken line on the* Mo *curve represents a zero-order reaction. Temp. of* Mo *filament* 464° *and of* W *filament* 560°.

FIG. 4.



The time for half decomposition of PH_3 *on* Mo *filament at* 570° *and* 645° *plotted against* p_{PH_3}.

If the reaction is of zero order, then on plotting log t against log p a straight line of unit slope should be obtained, whereas a unimol. reaction would give a line parallel to the log p axis since t is independent of press. Such a plot has been made in Fig. 3 from the results in Tables I and II

and some additional results not recorded. At higher press., the slope of the curve is unity, but gradually decreases until at 0·005 mm. it is nearly zero. The curve could not be extended to much higher press. since the half-life period would have been several hours. On the other hand, had the reaction rate been increased by raising the temp. of the filament, the order would have risen owing to evaporation of adsorbed PH_3, and consequently a much higher press. would be required to approach the zero-order reaction.

Temperature Coefficient.—The measurement of the temp. coeff. of the reaction, owing to its transitional character, allows of the estimation of two quantities. First, the energy of activation (E) of the reaction on the Mo surface can be calculated from the variation of $t_{\frac{1}{2}}$ with temp. by means of the formula $d \log (1/t_{\frac{1}{2}})/dT = E/RT$. The apparent energy of activation (Q) of the unimol. reaction is composed of two terms (see, *e.g.*, Hinshelwood, " Kinetics of Chemical Change in Gases," 2nd Edn., p. 228) : the energy of activation (E) on the surface minus the heat of desorption (λ) of adsorbed PH_3. Since Q is easily measured, λ can be calculated. In the transition reaction Q will vary between those limiting values. It has been seen that at the low press. of 0·005 mm. the reaction is not quite of the first order; hence, in determining the temp. coeff. two sets of expts. were made. In the first, the temp. of the filament was maintained const., the variation of half-life with press. plotted, and the curve extrapolated to zero press. Another similar series of observations was made for another temp., and the results extrapolated to $p_{PH_3} = 0$. The ratio of $t_{\frac{1}{2}}$ for the two temps. for $p_{PH_3} = 0$ was used to calculate Q.

Table III contains the data for this calculation, and Fig. 4 shows $t_{\frac{1}{2}}$ plotted against p_{PH_3}.

TABLE III.

Temp. of reaction tube 20°.

Temp. of filament 645°. Temp. of filament 574°.

Values of $p_{PH_3+H_2}$.

t.	Expt. 73.	Expt. 74.	Expt. 75.	Expt. 76.	Expt. 77.	Expt. 78.	Expt. 79.	Expt. 80.	Expt. 81.	Expt. 82.	Expt. 83.	Expt. 84.
0	0·0255	0·0445	0·1310	0·0580	0·0865	0·0610	0·0955	0·1365	0·0410	0·0117	0·0130	0·1090
1	0·0330	0·0515	0·1515	0·0685	0·1040	0·0660	0·1030	0·1465	0·0455	0·0133	0·0157	0·1145
2	0·0347	0·0575	0·1650	0·0775	0·1120	0·0695	0·1075	0·1515	0·0485	0·0157	0·0160	0·1175
3	0·0367	0·0605	0·1770	0·0805	0·1200	0·0735	0·1120	0·1585	0·0515	0·0160	0·0173	0·1220
4	0·0375	0·0635	0·1850	0·0845	0·1255	0·0760	0·1175	0·1625	0·0525	0·0163	0·0187	0·1265
5	—	0·0650	0·1915	0·0855	0·1270	0·0805	0·1215	0·1700	0·0540	—	—	0·1275
6	—	—	—	—	—	0·0810	0·1255	0·1735	—	—	—	0·1310
7	—	—	—	—	—	—	0·1280	0·1815	—	—	—	—

In expt. 84, 0·0385 mm. of H was present initially, and as seen from Fig. 4, $t_{\frac{1}{2}}$ lies on the curve, so H has no effect on the low-press. decomp.

The value of Q has been calculated from the curves in Fig. 4 at different PH_3 pressures, and it is seen that Q gradually increases with p_{PH_3}.

p_{PH_3}	0	0·02	0·06	0·10	0·20
R_1/R_2	2·00	2·24	2·61	2·79	2·80
Q (kg.-cal.)	15·1	17·5	20·8	22·3	22·3

Fig. 3 shows that at the lower temp., the reaction is not unimol., whereas at the higher temp., where PH_3 is much less strongly adsorbed, unimol. characteristics are more closely obeyed, *i.e.*, $t_{\frac{1}{2}}$ is nearly independent of p_{PH_3}.

Measurements of the temp. coeff. were also made at higher press. with the results given in Table IV.

TABLE IV.

Temp. of reaction tube 17°. Vol. of apparatus and filament as in Table I.

Expt.	p_{PH_3}.	$t_{\frac{1}{2}}$.	Temp. of filament.	Expt.	p_{PH_3}.	$t_{\frac{1}{2}}$.	Temp. of filament.
44	1·97	23	420°	49	1·92	1·35	497°
45	1·91	18	420	52	1·96	5·2	459
46	2·19	15	428	53	1·92	11·6	435
47	1·96	6·1	448				

Energy of activation $E = 39·3$ kg.-cal.

The heat of desorption of the PH_3 is thus $39·3 - 15·1 = 24·2$ kg.-cal. As this value is essentially calculated by extrapolation of the low-press. results to zero press., it represents the heat of desorption of the PH_3 from an uncovered surface of Mo.

Tungsten Filament.

W did not behave in the same way as Mo. The press. increase accompanying the comm decomp. was, however, exactly half the initial press. of PH_3. Similarly P was deposited as red variety on the walls of the tube. On carrying out expts. similar to those with the filament to determine whether white P was an intermediate product, some traces of it found; *e.g.*, in one expt., after the PH_3 (*ca.* 0·5 mm.) had been decomposed and the reac tube pumped out, on admission of a few mm. of O there was a bright flash of about 1 sec. durat There was no succeeding continuous glow and no change of press. The amount of whi produced by the filament was estimated to be less than 0·05 mm.

TABLE V.

Temp. of W filament, 560°; length of long filament, 12·0 cm.; length of short filament, 3·0 cm.

t.	$p_{PH_3+H_2}$.	p_{PH_3}.	k.	t.	$p_{PH_3+H_2}$.	p_{PH_3}.	k.	t.	$p_{PH_3+H_2}$.	p_{PH_3}.	k.
	Expt. 256.				Expt. 257.				Expt. 260.		
	Vol. 324 c.c.				Vol. 581 c.c.				Vol. 581 c.c.		
0	0·967	0·967	—	0	0·00855	—	—	0	0·1122	—	–
1	0·985	0·910	0·0262	1	0·00860	0·00845	—	1	0·1148	0·1070	0·02
2	1·003	0·875	0·0220	2	0·00915	0·00735	0·033	2	0·1183	0·1000	0·02
4	1·037	0·809	0·0195	4	0·00980	0·00585	0·041	4	0·1225	0·0916	0·02
8	1·100	0·701	0·0180	8	0·01080	0·00405	0·040	8	0·1303	0·0760	0·02
	$t/4 = 6·2$ min.				$t/4 = 2·8$ min.; $t'/4 = 1·6$ min.				$t/4 = 5·6$ min.; $t'/4 = 3·1$ m		
	Expt. 261.				Expt. 271.				Expt. 275.		
	Vol. 581 c.c.				Vol. 121 c.c.				Vol. 121 c.c.		
0	0·0412	—	—	0	29·0	—	—	0	262·5	—	–
1	0·0434	0·0368	0·049	1	30·3	26·4	0·041	1	276·0	235·5	0·05
2	0·0453	0·0330	0·048	2	31·2	24·6	0·035	2	283·0	221·5	0·05
4	0·0472	0·0292	0·038	4	33·3	20·4	0·038	4	294·0	199·5	0·05
8	0·0505	0·0226	0·033	8	37·0	13·0	0·043	8	311·5	164·5	0·05
$t/4 = 2·9$ min.; $t'/4 = 1·65$ min.				$t/4 = 3·4$ min.; $t'/4 = 9·1$ min.				$t/4 = 4$ min.; $t'/4 = 10·7$ m			
	Expt. 278.				Expt. 279.				Expt. 280.		
	Vol. 121 c.c.				Vol. 121 c.c.				Vol. 121 c.c.		
0	0·795	—	—	0	0·396	—	—	0	0·099	—	–
1	0·854	0·677	0·070	1	0·429	0·330	0·080	1	0·111	0·075	0·12
2	0·904	0·577	0·070	2	0·458	0·272	0·082	2	0·117	0·063	0·09
4	0·989	0·407	0·073	4	0·504	0·180	0·085	4	0·130	0·038	0·10
8	1·102	0·181	0·080	8	0·558	0·072	0·092	8	0·140	0·018	0·09
$t/4 = 1·7$ min.; $t'/4 = 4·5$ min.				$t/4 = 1·5$ min.; $t'/4 = 4·0$ min.				$t/4 = 1·0$ min.; $t'/4 = 2·6$ m			

In Table V the results of a series of runs are given in which the press. was varied from 0·0 to 262 mm. The vol. of the apparatus, including the particular manometric system in use, is shown; the time ($t/4$) required for the reaction to go 25% of its full extent is given at the bottom of the record of each expt. $t'/4$ is the value $t/4$ would have in an apparatus of 324 c.c. The obs. reaction velocity is due to the two filaments. In order to calculate the rate produced by the central portion of the long filament, $t/4$ must be increased by 4%. k is the unimol. velocity coeff. as in Table II.

First, it is noteworthy that $t/4$ does not markedly depend on press. A 30,000-fold press. increase changes $t/4$ by less than a factor of 10, *viz.*, from 1·6 to 10·7 min. The reaction is therefore nearly unimolecular, as is further shown by the constancy of k in each run. Further expts. were made with a press. of added H of the same order as that of the PH_3, but no inhibitory action was noticed either at high or at low press.

In Table VI are given two series of results with different filament temps., and at high (3 mm.) and low (0·05 mm.) press. The energies of activation (Q) are practically identical and therefore

TABLE VI.

Half-life	Temp. of filament.		Half-life	Temp. of filament.	
(sec.).	(1).	(2).	(sec.).	(1).	(2).
120	560°	441°	192	523°	407°
240	523	407	492	482	359
720	482	359	96	560	447
3000	415	—			
$Q = 25·8$ kg.-cal.			$Q = 23·8$ kg.-cal.		

in agreement with the fact that the reaction is unimolecular over this range of press. The temps. given in col. 3 were calculated by the old method of measuring the resistance and assuming a uniform temp. along the filament; those calculated by the new method are materially higher. The wide discrepancy is shown more clearly by a calcn. of the value of Q. The first and third results of the low-press. expts. give $Q = 28{\cdot}7$ kg.-cal., whereas the lower temp. gives $Q = 18{\cdot}7$ kg.-cal. Although the abs. value of the temp. and energy of activation of the reaction of the surfaces of filaments is not at present of great theoretical importance, yet the discrepancy may alter the significance of any theoretical discussions in comparing similar reactions catalysed by filaments of different materials.

Discussion.

The results may be summarised as follows. At low pressures, *i.e.*, less than 0·1 mm., phosphine decomposes according to a unimolecular law on tungsten and on molybdenum; the rate of reaction is unaffected by the presence of molecular hydrogen. No inhibitory influence of phosphorus can be detected for the simple reason that as soon as it leaves the filament it is removed from further possible action by condensation on the walls of the reaction tube. Further, the activities of the two catalysts appear to be of the same order of magnitude. As the pressure of the phosphine is increased, its adsorption on molybdenum increases rather more rapidly than on tungsten, so that with the former filament the reaction tends to be of zero order whilst the unimolecular law is still valid for the latter. In neither case is there any influence of hydrogen.

At the comparatively low temperatures at which these wires function, it is improbable that the evaporating hydrogen is anything but normal molecules, possessing an energy of translation corresponding to the temperature of the wire. Such a molecule is therefore unlikely to have sufficient energy to enable it to initiate a stable chain reaction between phosphine and oxygen. It is otherwise with the phosphorus. When P_4 molecules derived from white phosphorus condense on a cool surface, they do not in general condense to the red modification. Hence the molecules of phosphorus which evaporate from the filament cannot be normal P_4 molecules.

In a previous paper (Melville, *Proc. Roy. Soc.*, 1932, *A*, **138**, 394) mention has been made of an experiment in which normal P_4 molecules at low pressure are passed through a fine silica jet at 700° so as to dissociate them into P_2 molecules. That such molecules are actually formed by heating phosphorus vapour is shown, not only by density measurements (Preuner and Brockmoller, *Z. physikal. Chem.*, 1931, **81**, 159), but also by the appearance of an absorption band spectrum corresponding to P_2 molecules (Jakolewa, *Z. Physik*, 1931, 69, 548). A second cool jet defines a molecular beam which is projected into an evacuated tube provided at one end with a cool surface at − 80°. Condensation of the P_2 molecules gives rise to a red deposit. Now the temperature of the filaments in these experiments is sufficient to dissociate P_4 molecules. Further, in the experiments on the initiation of chains in phosphorus–oxygen mixtures by hot wires, it was observed that mere heating of a tungsten or molybdenum wire to 500° in phosphorus vapour produced a deposit of red phosphorus in the reaction tube. It may be concluded, therefore, in absence of evidence to the contrary, that P_2 molecules evaporate from a filament upon which phosphine molecules are being dissociated. The question then arises as to whether these P_2 molecules can initiate a chain reaction between phosphine and oxygen. This problem will be treated in a later paper.

There is, as might be expected, general similarity between the decomposition of ammonia and of phosphine. In accordance with the relatively greater stability of the former, the temperature to which the catalysts must be raised in order to obtain a measurable rate of reaction is rather higher for it than for phosphine; *e.g.*, on tungsten, phosphine at 500° has a half-life period similar to that of ammonia at 1000°, as found by Kunsman (*J. Amer. Chem. Soc.*, 1928, **50**, 2100; *Phil. Mag.*, 1930, **10**, 1015) in an apparatus of similar dimensions. Nevertheless, it is surprising that the decomposition of phosphine on tungsten is unimolecular at pressures where zero-order conditions obtain for ammonia. The ammonia is therefore much more strongly adsorbed. It would be of interest to compare the heats of evaporation (λ) of the two gases for the same filament by measuring the temperature

coefficient of the reactions over a wide range of pressures in order to find whether $\lambda_{PH_3} > \lambda$. At low pressures both reactions are unimolecular.

With molybdenum, both gases at high pressures decompose according to a zero-o law. No results for ammonia on this metal at low pressures are available, but in Kunsm results for ammonia on molybdenum at different temperatures, a plot of the logarithm o time required for half-decomposition against the reciprocal of the absolute tempera gives a curve which shows a decrease in the apparent energy of activation at high t peratures. This curvature is possibly due to the smaller adsorption of the gas, whereby order of the reaction increases from zero to unity.

One important difference between phosphine and ammonia is that hydrogen does inhibit the decomposition of the former, whereas with the latter inhibition is pronou both at high and at low pressures. If the surface of the catalyst is catalytically uni and if the inhibitory effect of hydrogen on ammonia is merely due to displacement of adsor ammonia, then absence of inhibition by hydrogen on phosphine is not to be expec There are two alternative explanations of this discrepancy : (*a*) the catalyst is not of uni activity and the ammonia decomposes on centres which can be easily covered with hydro whereas different active centres for phosphine are not affected by hydrogen; (*b*) hydro not only displaces ammonia, but after or as a consequence of being adsorbed it beco sufficiently reactive to attack the intermediate products of the decomposition of ammonia molecule and to regenerate this gas. In the second case inhibition by hydro would then be due essentially to a chemical reaction, and therefore it is reasonable suppose that there would be a marked difference in the condition for the appearanc inhibition.

The energies of activation (E) for the decomposition of ammonia on tungsten, mol denum, and nickel are all of the same magnitude, *viz.*, 45 kg.-cal., which is much hig than the values for phosphine. Although, in general, there is no connexion betw activity of catalyst and E, yet it happens that tungsten and molybdenum are much mo active for phosphine than for ammonia, *i.e.*, increased activity is associated with a l energy of activation.

Summary.

The decomposition of phosphine has been studied on the surface of tungsten a molybdenum filaments at pressures from 0·01 to 300 mm. Reaction velocity is measur at about 500°. On tungsten, the order of the reaction is nearly unity and is not mu affected by pressure. On molybdenum, the decomposition is unimolecular at low pressur but becomes of zero order as the pressure is increased. The heat of adsorption of ph phosphine has been calculated from the temperature coefficient of the reaction at high a at low pressures. The products of the reaction are red phosphorus and hydrogen. Mol cular hydrogen has no effect. These reactions have been compared with the correspondi ammonia reactions.

A simple method of correcting for end losses in a hot filament is described.

The authors are indebted to Dr. E. B. Ludlam for encouragement during the work, and t the Carnegie Trustees for a scholarship (H. W. M.).

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The Diffusion Coefficients of Bromine-Argon, Bromine-Methane, Bromine-Hydrogen Chloride, Bromine-Nitrous Oxide

By John E. Mackenzie, D.Sc., and
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XIX.—The Diffusion Coefficients of Bromine-Argon, Bromine-Methane, Bromine-Hydrogen Chloride, Bromine-Nitrous Oxide.

By **John E. Mackenzie**, D.Sc., and **Harry W. Melville**, Ph.D.

(MS. received June 19, 1933. Read July 3, 1933.)

In a previous communication (*Proc. Roy. Soc. Edin.*, vol. lii, 1932, p. 337) a visual method of measuring the diffusion coefficients of $Br_2 : H_2$, $Br_2 : N_2$, $Br_2 : O_2$, and $Br_2 : CO_2$ was described. The investigation has been extended to include similar measurements for bromine diffusing into argon, nitrous oxide, methane, and hydrogen chloride. Preliminary experiments in which a photoelectric cell replaces the human eye have also been made and confirmatory results have been obtained.

Experimental.

The apparatus (*cf.* fig. 1, *loc. cit.*, p. 339) previously used was modified by sealing on to the upper end of the diffusion tube a **T**-tube provided with two glass taps in place of the rubber stopper and glass tap. This arrangement allowed of the diffusion tube being alternately evacuated and filled with gas (argon, methane, etc.). The repetition of the process two or three times ensured the gas in the tube being free from air.

The procedure was also modified in that after the diffusion tube had been filled with gas, a small gas-wash bottle containing just enough concentrated sulphuric acid to cover the end of the outlet tube was attached to one limb of the **T**-tube. The pressure exerted by the bromine and later by the bromine vapour was relieved by gas escaping through the sulphuric acid and the diffusion went on at atmospheric pressure. Thus the calculation of the mean value of the pressure of the bromine vapour as required in the earlier experiments (*loc. cit.*, p. 342) became unnecessary.

The argon and nitrous oxide were obtained from the British Oxygen Company and from Elliot & Company. The argon was stated to contain from 0·5 to 1 per cent. of nitrogen and the nitrous oxide to have not more than 0·2 per cent. impurity. Methane was prepared by the sodium acetate-soda lime method. It was collected over water and purified by repeatedly passing it through concentrated sulphuric acid, bromine, and potassium hydroxide solution to free it from unsaturated

hydrocarbons, carbon dioxide, etc. Water vapour was removed by phosphorus pentoxide.

Hydrogen chloride was generated in a Kipp's apparatus from ammonium chloride and sulphuric acid and dried by concentrated sulphuric acid and phosphorus pentoxide. The gas was passed into and through the diffusion tube until on issuing from the tube it showed complete absorption by water.

Visual Method.

In Table I and in fig. 1 the complete results are given for a few typical experiments. The calculation of the diffusion coefficient was carried out

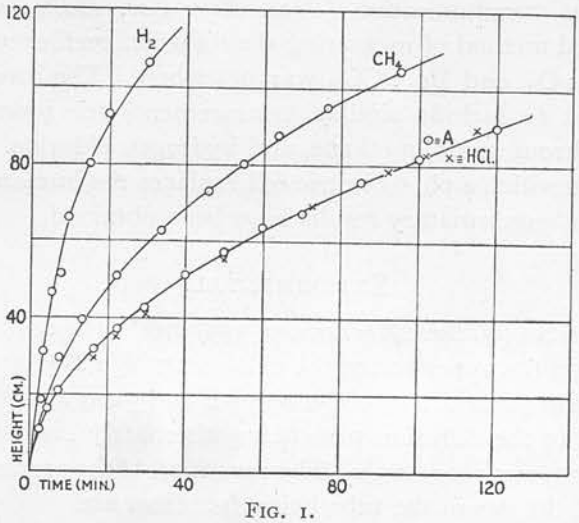

Fig. 1.

as before (*loc. cit.*) and the results are given in Table II. Two experiments with CO_2 and with H_2 are also included for comparison with those in the first paper. These experiments were made by different observers, and it will be noticed that the results agree very well with those obtained previously. A comparison of the rates of diffusion of bromine into nitrous oxide and into carbon dioxide was also made, but no difference could be detected. This is to be expected, as the diffusion coefficients are almost identical, $D_{Br_2-N_2O}=0{\cdot}110$ and $D_{Br_2-CO_2}=0{\cdot}107$. The calculated values of D are again all consistently higher than the observed figures.

Photoelectric Method.

It was thought necessary, therefore, in spite of the concordance of these results, to obtain independent confirmation by another method. Experiments were performed in which a photoelectric cell was employed

TABLE I.

Br_2–A. Time in mins.	Height in cm. (x).	Br_2–CH_4. Time.	x.	Br_2–HCl. Time.	x.	Br_2–H_2. Time.	x.	Br_2–CO_2. Time.	x.
1	8·5	1	9·0	2	11·0	1	18·0	1	8·0
2	10·5	3	18·0	5	18·0	2	25·0	2	11·0
4	15·5	7	29·5	8	21·5	3	31·0	7	20·5
7	21·0	13	39·5	16	30·0	4	40·0	10	25·0
11	27·0	22	51·0	22	35·5	5	46·0	20	36·0
16	32·0	34	63·0	30	41·0	7	51·5	30	44·5
22	37·0	46	73·0	42	47·0	10	66·0	40	51·0
30	43·0	55	80·0	50	55·0	15	80·0	60	63·0
40	51·0	64	87·5	74	69·0	20	93·0	75	70·0
50	57·0	77	95·0	92	78·0	30	107·0	100	80·0
60	63·0	95	105·0	102	83·0			120	88·0
70	67·5			114	89·0				
85	75·0								
100	81·5								
120	89·5								
Atmos. press. .	742 mm.	744		769		755		755	
Temp. . .	16° C.	16°		15°		16·5°		16·5°	
V.P. (liquid bromine).	144 mm.	144		137·5		147		147	
σ_A . .	$1·66 \times 10^{-8}$ cm.	σ_{CH_4}	$1·53 \times 10^{-8}$	σ_{HCl}	$1·47 \times 10^{-8}$	..		..	
Date . .	2.2.33	10.2.33		13.2.33		3.2.33		3.2.33	

TABLE II.

Gas Mixture.	x (cm.).	Time (min.).	D cm.^{2} sec.$^{-1}$.	D_{760}.	$D_{calc.}$
Br_2–A	36	20	0·0862	0·0846	
	62·5	60	0·0861	0·0848	0·108
	89·5	120	0·0897	0·0876	
Br_2–CH_4	30	7·5	0·1596	0·1563	
	60	30·5	0·1571	0·1538	0·175
	90	69·5	0·1586	0·1553	
Br_2–HCl	55	50	0·0820	0·0830	
	67	70	0·0853	0·0863	0·125
	83	102	0·0898	0·0908	
Br_2–H_2	46	5	0·563	0·560	
	66	10	0·580	0·575	0·598
	102	25	0·554	0·550	
Br_2–CO_2	46	20	0·0860	0·0854	
	66	70	0·0879	0·0873	0·107
	102	120	0·0859	0·0853	

to measure the concentration of bromine vapour. Fig. 2 presents a plan and elevation of the apparatus adjoining the diffusion tube, and fig. 3 is a diagram of the electric circuit.

The diffusion tube (D) used in the above experiments was attached to a system of pulleys and gear wheels to permit of its being moved vertically. The photoelectric cell (C), slits (S_1 and S_2), and source of illumination (L) were mounted on a fixed platform (F), through which the diffusion tube could be raised or lowered. The widths of S_1 and S_2 were respectively 0·5 and 1·5 mm. A helium-filled potassium cell proved to be most suitable, as it is sensitive to the light absorbed by bromine. The photoelectric current was amplified by a valve (V) (Osram L.210). In the anode circuit there was a sensitive milliammeter (G), connected in parallel with a potentiometer system to balance out the anode current when the cell was not illuminated. If the valve is worked on the straight portion of the anode current/grid volts curve without running into grid current, and if the photoelectric current in the cell is proportional to the intensity of the light falling upon it, the reading of the milliammeter will be directly proportional to the intensity of illumination. In the present case these conditions were maintained as nearly as possible.

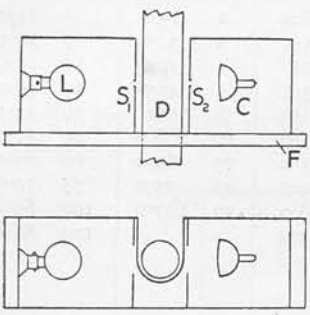

FIG. 2.

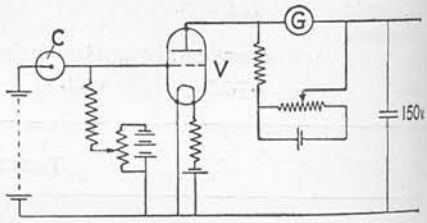

FIG. 3.

The results were calculated in the following way:—

Let I_0 and I be the intensities of the emergent beam from the empty tube and from the tube containing bromine vapour at a pressure p, then

$$I = I_0 e^{-kp}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is a constant depending only on the extinction coefficient of Br_2 and on the dimensions of the tube. When the deflection of the anode milliammeter is proportional to the intensity of the light entering the cell,

$$ln i/i_0 = -kp, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where i = current at Br_2 pressure p.

i_0 = ,, ,, ,, nil.

Now

$$ln p_1/p_2 = x^2/2Dt, \quad . \quad . \quad . \quad . \quad (3)$$

where p_1 and p_2 are the pressures of Br_2 at the surface of the liquid bromine

and at a height x cm. above it, after t sec. If the corresponding currents are i_1 and i_2, then combining equations (2) and (3)

$$ln\left(\frac{lni_0/i_1}{lni_0/i_2}\right)=\frac{x^2}{2Dt}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Table III gives the results for Br_2–CO_2.

TABLE III.

Temp. 20° C.

Height of Slit above Liquid Bromine (cm.).	Time of Diffusion (min.).	i_2.	i_1.	i_0.	D_{760}.
23·6	20	1·030	0·080	1·225	0·083
33·6	23	1·190	0·080	1·225	0·084
18·6	34	0·470	0·080	1·200	0·080
23·6	36	0·700	0·080	1·200	0·081

The values of D_{760} agree fairly well with those obtained by the visual method (*cf.* Table II). Further detailed results have not been given as these experiments are intended only to verify the previous results. It is hoped, however, by making a number of improvements in the photoelectric cell apparatus and in the accurate thermostating of the diffusion tube, to study in detail the variation of D with the composition of the mixture and with the total pressure.

The authors thank Messrs Brockie, Wood, Gray, and Thompson for assistance in some of the experiments.

SUMMARY.

The diffusion coefficient of Br_2–A, Br_2–CH_4, Br_2–HCl, and Br_2–N_2O have been determined by a visual method.

Preliminary experiments, in which photoelectric measurements replace those made visually, are described. The results thus obtained confirm those got by the visual method.

(*Issued separately September* 1, 1933.)

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THE INHIBITION OF THE PHOTOCHEMICAL DECOMPOSITION OF AMMONIA BY ATOMIC HYDROGEN.

By H. W. Melville.

Received 20th October, 1932.

It is now well recognised that molecules which exhibit diffuse absorption band spectra undergo dissociation on absorption of a quantum of radiation in a time much less than the interval between collisions at atmospheric pressure. Bonhoeffer and Farkas[1] pointed out that, owing to the nature of its absorption spectrum, the photo-decomposition of ammonia would involve the primary dissociation of the molecule into NH_2 and H. They showed that the absence of fluorescence of the NH_3 molecules was in accordance with this view. Several experiments were later carried out to prove the existence of hydrogen atoms during the decomposition of ammonia.

Farkas, Haber and Harteck[2] found that if ammonia is mixed with hydrogen and oxygen and illuminated with a zinc spark, combination of H_2 and O_2 occurs. At temperatures below 415° C. many molecules of H_2O were formed per NH_3 molecule decomposed, while explosion occurred above 415° and 300 mm. pressure, although H_2 and O_2 alone require to be heated to at least 440° for spontaneous explosive combination. Haber and Oppenheimer's observation[3] that H atoms induce explosion in $H_2 - O_2$ mixtures below 440° appeared to indicate that the ammonia sensitised reaction must be due to initiation by H atoms.

Taylor and Emeléus[4] discovered that just as atomic hydrogen, produced by the reaction $Hg(2^3P_1) + H_2$, induced polymerisation in ethylene, so on illuminating a $NH_3 - C_2H_4$ mixture polymerisation of the hydrocarbon took place. The products of the reaction, however, contained a considerable amount of nitrogenous substance. Hill and Vernon[5] found that tungstic oxide was rapidly reduced in presence of illuminated ammonia.

These experiments are based upon analogy, and although they are very convincing on account of the simple molecular transformations involved, yet they are not direct proofs of the existence of atomic hydrogen since the part played by the reactive radical NH_2 has been neglected.

[1] *Z. physik. Chem.*, **134**, 337, 1928.
[2] *Z. Electrochem.*, **36**, 711, 1930.
[3] *Z. physik. Chem.*, **16B**, 443, 1932.
[4] *J. Amer. Chem. Soc.*, **53**, 562, 1931.
[5] Cited by Taylor and Emeléus, *unpublished experiments*.

The second problem in the photochemistry of ammonia w required a direct proof was the low quantum yield. In a recen cussion of the question Wiig and Kistiakowski [6] conclude that most plausible explanation is recombination of the primary pro of dissociation either by ternary collisions or at the walls. They su that surfaces prepared in a suitable way may inhibit or accelerate recombination.

Similar problems arose during experiments on the photochem of phosphine. The absorption spectrum is of the predissoci type [7] and the quantum yield is less than unity.[8]

In the mercury photosensitised decomposition of phosphine presence of hydrogen a simple mechanism leads to the equation

$$1/R = 1/K\left(1 + \frac{k_2[H_2] + k_3}{k_1[PH_3]}\right),$$

R is the rate of decomposition, K is a constant, k_1 is the reac velocity coefficient of PH_3 with 2^3P_1 Hg atoms, k_2 that for H_2 an the rate of deactivation of excited Hg atoms by radiation. On plot $1/R$ against $[H_2]$, maintaining $[PH_3]$ constant, a straight line sh be obtained. For low values of $[H_2]$ a linear relationship held g but as $[H_2]$ increased the curve began to tend upward, becoming con to the $[H_2]$ axis. That is, the reaction velocity decreases at a rate wh is greater than can be accounted for by simple deactivation of the cited mercury atoms by molecular hydrogen. Since atomic hydro is produced by this deactivation process it was natural to assume th H atoms were responsible and that the retardation was due to t reaction $PH_2 + H$ being accelerated owing to the artificial increa in the concentration of H atoms.

This tentative suggestion was verified by illuminating a PH_3-H mixture separately and simultaneously with a zinc spark and a wat cooled mercury arc lamp. The rate of decomposition with simultaneo illumination by spark and arc was less than that with separate illumin tion, which proved that in presence of atomic hydrogen the pho dissociation of PH_3 was inhibited. At the low pressures used t recombination $PH_2 + H$ must occur at the walls.

On recalculating Mitchell and Dickinson's results [10] on the mercur photosensitised decomposition of ammonia according to the abo equation it was found that curves similar to those for phosphine we obtained as is shown by Fig. 1. This parallelism suggested that confirmatory experiment might be made on the same basis as that f phosphine.

A zinc spark and a water-cooled mercury lamp were therefore se up close to a 7 cm.-diameter silica bulb attached to a McLeod gauge liquid air traps, pumps and gas * reservoirs. The relative distanc of spark and arc was so adjusted that the rates of the direct and photo sensitised reactions in absence of hydrogen were about equal. Sufficien hydrogen to reduce the rate of the photosensitised reaction to a negligibl small value was then introduced. The rate of the direct reaction is not

[6] *J. Amer. Chem. Soc.*, **54**, 1906, 1932. [7] Melville, *Nature*, 129, 546, 193
[8] Melville, *unpublished experiments*.
[9] Melville, *Proc. Roy. Soc.*, A **138**, 374, 1932.
[10] *J. Amer. Chem. Soc.*, **49**, 1487, 1927.
* The gases were saturated with mercury before entering the reaction bulb.

affected by molecular hydrogen, the experiments being made at room temperature. First of all the mixture is illuminated with the zinc spark and, after condensing out the ammonia with liquid air, the pressure of $N_2 + H_2$ measured. The arc is then switched on and, keeping the spark intensity constant, another exposure made of the same period, the pressure of $N_2 + H_2$ being again determined.

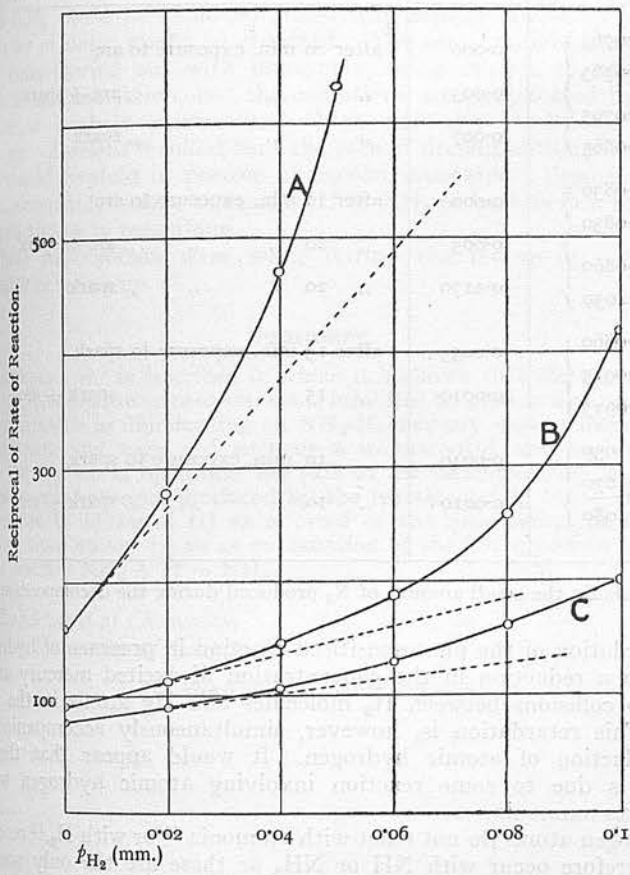

FIG. 1.—Mitchell and Dickinson's results for the photosensitised decomposition of NH_3. The curves show that the reciprocal of the rate of decomposition increases more rapidly than p_{H_2}, the deviation being relatively greater at low NH_3 pressures.

$A = pNH_3 = 0{\cdot}96$ mm.
$B = pNH_3 = 1{\cdot}88$ mm.
$C = pNH_3 = 3{\cdot}22$ mm.

The results of four typical series of experiments are shown in the Table below. When the mixture of ammonia and hydrogen is exposed to the arc alone, there is no pressure change and therefore no decomposition of ammonia. On illuminating the mixture with arc and spark simultaneously the pressure increase, *i.e.*, the pressure of $N_2 + H_2$ produced, is *less* than that with spark alone. The direct photochemical decomposition of ammonia is consequently retarded when the arc is switched on.

TABLE I.

Pressure of NH_3, 0·3 mm. Room Temperature *ca.* 20° C.
Rate of Hg sensitised reaction 0·0125 mm. $N_2 + H_2$ per 20 min. in absence of

p_{H_2} mm.	Increase of Press.	Condition of Illumination.
0·0765	0·000	after 20 min. exposure to arc
0·0765	0·003	,, ,, ,, ,, arc + spark
0·0795		
0·0865	0·007	,, ,, ,, ,, spark
0·0830	0·000	after 10 min. exposure to arc
0·0830	0·003	,, 20 ,, ,, ,, arc + spark
0·0860		
0·1030	0·0170	,, 20 ,, ,, ,, spark
0·0860	0·0055	after 15 min. exposure to spark
0·0915	0·0010	,, 15 ,, ,, ,, spark + arc
0·0925		
0·1030	0·0040	,, 10 min. exposure to spark
0·1070	0·0010	,, 10 ,, ,, ,, spark + arc
0·1080		

p_{H_2} includes the small amount of N_2 produced during the decomposition.

Retardation of the photosensitised reaction in presence of hydrog is due to a reduction in the concentration of excited mercury atom owing to collisions between H_2 molecules and Hg atoms in the 2^3 state. This retardation is, however, simultaneously accompanied b the production of atomic hydrogen. It would appear that the in hibition is due to some reaction involving atomic hydrogen whic regenerates ammonia.

Hydrogen atoms do not react with ammonia [11] or with N_2,[12] reaction must therefore occur with NH or NH_2 as these are the only possible intermediate products of the decomposition in a static system.[4, 13] It is simpler to assume, having regard to the fact that molecular hydrogen is without influence on the reaction at 20° C., that retardation is due to the reaction $NH_2 + H = NH_3$, which occurs either by the participation of a third molecule or on the walls of the insolation tube in order to effect stabilisation of the NH_3 molecule.

Since the primary photo-dissociation of NH_3 can be represented by the equation $h\nu + NH_3 = NH_2 + H$, and as the above experiments indicate that the reverse reaction also occurs, then it is probable in absence of artificially introduced H atoms, *i.e.*, during the normal photo-reaction, the same reaction $NH_2 + H \rightarrow NH_3$ takes place. Hence

[11] Bonhoeffer and Boehm, *Z. physik. Chem.*, **119**, 385, 1926.
[12] Lewis, *J. Amer. Chem. Soc.*, **50**, 27, 1928.
[13] Gedye, *J. Chem. Soc.*, 1160, 1932.

It may be concluded (*a*) that the low quantum yield in the direct decomposition of NH_3 is due to recombination of the primary products of dissociation, (*b*) that the inhibition by H atoms provides an additional direct proof that H atoms are one of the intermediate products of the reaction.

It is convenient in this communication to mention that the recombination hypothesis may be supported in another direction. If H or NH_2 could be removed sufficiently rapidly quantum yields of the order of unity might be obtained. The corresponding experiments have been carried out with phosphine, using oxygen to remove the products of dissociation, but the conditions are complicated by the intrusion of a chain mechanism. With ammonia conditions are less complex. Emeléus [14] found that the rate of decomposition of ammonia is increased twofold in presece of carbon monoxide. Presumably the carbon monoxide is able to remove H or NH_2 or both before they have an opportunity to recombine.

These experiments were made during the tenure of a Carnegie Research Scholarship.

Summary.

An experiment is described in which it is shown that the direct photochemical decomposition of ammonia is inhibited by atomic hydrogen. The method consists in illuminating an NH_3-H_2-mercury vapour mixture with a zinc spark and with and without a water-cooled mercury arc lamp. With the Hg arc in operation the rate of the decomposition is retarded by the atomic hydrogen produced by the reaction (2^3P_1) $Hg + H_2$. This experiment is advanced (1) as a proof of the dissociation of ammonia into hydrogen atoms, (2) as an explanation of the low quantum yield due to the reaction $NH_2 + H = NH_3$.

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[14] *These Transactions*, **28**, 89, 1932.

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The Photochemistry of Phosphine.

BY H. W. MELVILLE.

[*Reprinted from the* PROCEEDINGS OF THE ROYAL SOCIETY, A, Vol. 139.]

The Photochemistry of Phosphine.

By H. W. MELVILLE.

(Communicated by J. Kendall, F.R.S.—Received October 1, 1932.)

Introduction.

In the previous paper in this investigation* the first part (I) dealt with the mercury photo-sensitized decomposition of phosphine, and the second (II) with the sensitized photo-oxidation. Certain calculations and conclusions in that paper had to be left unfinished, until data on the direct photochemical reaction became available. The present paper, therefore, is devoted to the absorption spectrum, the direct decomposition and the photochemical oxidation of phosphine. The experiments are to some extent confirmatory of those involving excited mercury atoms but, owing to the simpler conditions obtaining in the direct reaction, it is possible to extend the calculations on the results to yield more information about the mechanism of the reactions.

* 'Proc. Roy. Soc.,' A, vol. 138, p. 374 (1932).

Part III.

The Absorption Spectrum of Phosphine.

The absorption spectrum has been photographed by Purvis* using a condensed cadmium spark. In a 10 cm. tube absorption begins at 223 mμ at room temperature, and at 100° C. the limit is raised to 224 mμ. No bands were observed.

Owing to the discontinuous nature of the cadmium spectrum, it was deemed advisable to photograph the absorption spectrum, using a continuous source of radiation.

The source of light was a water-cooled hydrogen tube consuming about 2 kw., while the spectroscope was a small Hilger instrument giving the region 200–800 mμ on a quarter-plate. Two absorption tubes were used, one 110 cm. long of glass and fitted with quartz windows, the other entirely of fused silica 15 cm. long. Exposures ranged from 1 minute to 1 hour, using Wellington Anti-screen plates.

A series of exposures of about 1 hour was made at room temperature with pressures of phosphine from 0·01 mm. to 760 mm. with the 110 cm. tube. At atmospheric pressure absorption was continuous beyond 225 mμ as far as 185 mμ, the limit of the spectroscope. Preceding this continuous absorption, four very weak diffuse absorption bands could be observed at wave-lengths of 228, 229·5, 232 and 236 mμ. The breadth of the bands was 1–2 mμ, but no fine structure was evident. The dispersion of the spectroscope was sufficient to show structure, had there been any present, for the rotational lines in the Schumann O_2 bands could be distinguished. When the pressure of the phosphine was reduced to 20 mm. the limit of continuous absorption had moved to about 217 mμ, while all trace of the bands observed at atmospheric pressure had disappeared. Upon reducing the pressure to 0·01 mm., the absorption limit became rather indefinite, but no light was transmitted beyond 195 mμ. No bands appeared on the plates except those belonging to the O_2 molecule.

Using the 15 cm. tube the absorption spectrum was photographed at 300° C., at which temperature the limit of continuous absorption shifted slightly—1–2 mμ—towards the red, while all traces of band absorption observed at room temperatures had disappeared.

These experiments would therefore indicate that the absorption spectrum of phosphine is of the predissociation type and similar to that of ammonia.

* 'Proc. Camb. Phil. Soc.,' vol. 21, p. 566 (1923).

The Direct Photochemical Decomposition. Materials and Apparatus.

The phosphine and other gases used in these experiments were prepared as described in I.

The apparatus is shown diagrammatically in fig. 1. It consisted of a McLeod gauge (M) attached to a liquid air trap (T_4) provided with a tap and a reaction bulb of silica (R_1), 7 cm. in diameter. This bulb was connected to the apparatus by a silica-glass ground joint so that the bulb could be rotated. When working

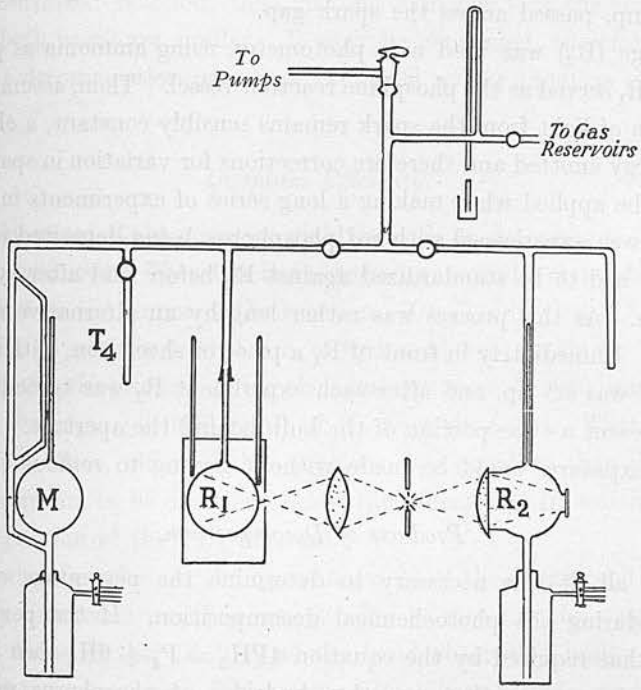

FIG. 1.

at temperatures above 15° C. the bulb was surrounded by an electric furnace provided with a small window. Two silica thermometers were used for reading temperatures. To the other end of the vacuum line another McLeod gauge, fitted with a liquid air trap was sealed. The bulb of this gauge functioned as a reaction tube and was fitted with a quartz lens 6 cm. in diameter and focal length (for yellow light), 10 cm. at one side and a quartz plate at the other. The whole was placed in a brass box fitted with a suitable window for observing the capillary so that, if necessary, water at a constant temperature could be circulated through it. The reasons for constructing the gauge in this manner were (1) compactness and ease of temperature control, (2) economy

of quartz plates and lenses, (3) sensitivity, owing to the fact that no expansion takes place from the reaction tube into the bulb of the McLeod gauge. The bulb of this gauge was about 300 c.c. in volume.

The apparatus was exhausted by a mercury condensation pump backed by an oil pump. The spark was placed in between R_1 and R_2: it was fed from a 10 K.V.A. 6600 volt transformer with suitable condensers across the secondary. The electrodes were of zinc and aluminium, and were kept cool by a strong blast of air. The spark voltage was usually about 3000 when a current of about 1 amp. passed across the spark gap.

The gauge (R_2) was used as a photometer, using ammonia as photometric gas, while R_1 served as the phosphine reaction vessel. Then, assuming that the distribution of light from the spark remains sensibly constant, a check is kept on the energy emitted and therefore corrections for variation in spark intensity can easily be applied when making a long series of experiments in R_1.

Trouble was experienced with red phosphorus being deposited on the walls of R_1. R_1 had to be standardized against R_2 before and after every experimental run. As this process was rather lengthy an alternative method was employed. Immediately in front of R_1 a piece of sheet iron, with an aperture 2×1 cm., was set up, and after each experiment R_1 was turned on its axis so as to present a clear portion of the bulb behind the aperture. In this way about 15 exposures could be made without having to remove the bulb for cleaning.

Products of Decomposition.

First of all, it was necessary to determine the percentage of hydrogen produced during the photochemical decomposition. If the percentage approached that required by the equation $4PH_3 = P_4 + 6H_2$ then it would be reasonable to assume that no other hydrides of phosphorus were formed. Table I is a record of a series of experiments carried out at room temperature with a zinc spark, the exposure time being about 20 minutes.

Table I.

p_{PH_3} mm.	$p_{PH_3} + p_{H_2}$ after exposure.	$p_{H_2} + 0{\cdot}0085$ mm.	p_{PH_3} decomp.	H_2, per cent. of theory.
0·1455	0·1465	0·0123	0·0028	91
0·0788	0·0815	0·0207	0·0087	93
0·1245	0·1290	0·0263	0·0133	90
0·0645	0·0690	0·0235	0·0105	95
0·0930	0·0980	0·0275	0·0140	91
0·1345	0·1465	0·0495	0·0290	95
			Average	93

0·0085 mm. is the vapour pressure of phosphine, measured by the McLeod gauge, at the temperature of the liquid air employed in this series. The slightly low value of the percentage of hydrogen is, no doubt, due to adsorption of the hydrogen atoms by the walls of the reaction tube. The phosphorus is deposited as a brownish-red film. In view of the probability that the reactions subsequent to the primary fission of the PH_3 molecule take place on the walls (see below), it would appear that no phosphorus vapour is produced. It is important to observe that 93 per cent. agrees well with 95 per cent. found in the photo-sensitized reaction, thus yielding evidence that the secondary reactions in both cases are similar. It may be concluded, therefore, that the result of the decomposition process is expressed by the equation given above.

Quantum Efficiency.

The measurement of the quantum yield depends on determining the pressure of hydrogen produced. Therefore it was necessary to find if molecular hydrogen had any effect on the course of the reaction. On illuminating 0·0785 mm. of PH_3 in R_1 for 20 minutes 0·0045 mm. of hydrogen were obtained. On adding 0·0660 mm. of hydrogen and giving the same exposure, 0·0040 mm. (accuracy of pressure readings $\pm$0·0005 mm.) of H_2 were produced. That is, H_2 had practically no effect, although the pressure was equal to that of the PH_3. In the experiments to be described below the pressure of H_2 was invariably a very small fraction of the PH_3 pressure.

Since Warburg's value for the quantum yield of the decomposition of NH_3 has recently been confirmed,* it was decided to measure the quantum yield for PH_3 in terms of that of NH_3 as the band absorption limits are almost identical for the two gases. The group of lines near 210 mμ emitted by the zinc spark is absorbed completely by NH_3 and by PH_3 if the pressure is sufficiently high.

Preliminary experiments were made to ascertain when NH_3 or PH_3 in R_1 began to transmit the zinc lines appreciably ; it was found that at about 30 mm. incomplete absorption became noticeable. Pressures of 100 mm. were therefore employed. R_1 and R_2 were filled with NH_3 at 100 mm. and an exposure of 10–20 minutes given, after which the pressure of $N_2 + H_2$ was determined by condensing out the NH_3 with liquid air. PH_3 at 100 mm. was then put into R_1 and the same procedure repeated. Table II gives three series of experi-

* Wiig and Kistiakowski, ' J. Amer. Chem. Soc.,' vol. 54, p. 1906 (1932).

ments with the 7 cm. bulb for R_1 at room temperature, while Table III is a record of two series with a 2 cm. cylindrical tube 15 cm. long.

Table II.

Spark.	Gas in R_1.	p in R_1 (mm.)	$p_{H_2+N_2}$ (R_2)	γ.
Al	NH_3	0·0143	0·0412	—
	PH_3	0·0145	0·0250	0·61
	PH_3	0·0190	0·0250	0·80
	PH_3	0·0183	0·0369	0·52
Zn	NH_3	0·0125	0·0203	—
	PH_3	0·0165	0·0209	0·47
	PH_3	0·0195	0·0203	0·57
	PH_3	0·0180	0·0203	0·53
Zn	NH_3	0·0770	0·0209	—
	PH_3	0·0685	0·0119	0·58
	NH_3	0·1290	0·0459	—

In the third series of Table II the bulb was not rotated. This series was carried out after an interval of 6 months, during which time the bulb had been in continuous use. Another series of experiments also carried out at a different time yielded the resulls $\gamma = 0{\cdot}57, 0{\cdot}57, 0{\cdot}50$. For the 7 cm. bulb the average value of γ is 0·56.

Table III.—2 cm. Cylindrical Tube. Temperature 18° C. Zn spark.

Gas in R_1.	$p_{H_2+(N_2)}$ in R_1.	$p_{H_2+N_2}$ in R_2.	γ.
NH_3	0·0790	0·0152	0·47
PH_3	0·0940	0·0244	
NH_3	0·0130	0·0304	
NH_3	0·0975	0·0292	0·52
PH_3	0·0520	0·0143	
NH_3	0·0455	0·0351	
NH_3	0·1560	0·0298	0·47
PH_3	0·0915	0·0167	
NH_3	0·0505	0·0188	

In the experiments recorded in Table III rotation of the tube was not practicable, so that ammonia calibration experiments were made before and after every phosphine experiment. The mean of the ammonia experiments was used for calculating the quantum yield. The insolation tube was cleaned

out with bromine water after each series in order to remove the film of red phosphorus deposited on the window.

It will be observed that the quantum yield in the smaller vessel is a little less than that in the 7 cm. bulb, thus confirming the results of the photo-sensitized experiments.

A possible criticism may be levelled against the interpretation of the increase in the rate of the photo-sensitized decomposition in wider tubes. In a recent paper on the mean life (τ) of the mercury atom in the $2\,^3P_1$ state, Garrett* finds that the pressure of the mercury vapour in a tube 3 cm. in diameter has quite a large influence on the *apparent* mean life. The apparent mean life is the life measured by the apparatus employed by Garrett. For example, at 10^{-4} mm. τ is $1{\cdot}43 \times 10^{-7}$ second, and at 10^{-5} mm., $1{\cdot}08 \times 10^{-7}$ second. This increase in life is due to part of the resonance radiation being reabsorbed by the mercury vapour before escaping out of the tube in which the mercury atoms are excited. Extrapolation of Garrett's results to 0·001 mm., which pressure was used in the photo-sensitized experiments, gives a value of τ approximately equal to 5×10^{-7} seconds. At 0·001 mm. therefore, the apparent mean life of Hg $2\,^3P_1$ will increase with the diameter of the tube, but as k_3 (see I) is inversely proportional to τ, the ratio k_1/k_3 will increase with diameter. Hence the observed increase in k_1/k_3 may possibly be due to this increase in apparent life by reabsorption of resonance radiation. Garrett's results, however, only apply to pure mercury vapour; that is, when gas phase deactivation occurs by radiation alone. When phosphine is present, the *effective* mean life is much smaller and is proportional to $1/(k_1[PH_3] + k_3)$. In the 2 cm. tube $k_1/k_3 = 2{\cdot}7$, while the pressures used for determining the ratio k_1/k_3 were in the range 0·5–10 mm. At the low pressure of 1 mm. then, the mean life is $k_3/(k_1[PH_3] + k_3) = 1/4$ that in absence of phosphine, or 10^{-7} second. The effective life is thus equal to the mean life at low pressure ($<10^{-5}$ mm.) of mercury vapour so that little reabsorption of resonance radiation could occur.

Furthermore, had appreciable reabsorption of resonance radiation taken place, the line obtained by plotting the reciprocal of the reaction rate (1/R) against the reciprocal of the phosphine pressure should have become concave to the $1/p_{PH_3}$ axis at high values of $1/p_{PH_3}$, owing to the increase in $[Hg^1]$. The line in fig. 5 of Paper I shows no such deviation. In order to settle the matter, more accurate data than the extrapolated value used above would be

* 'Phys. Rev.,' vol. 40, p. 779 (1932).

required on the apparent mean life in mercury vapour at 0·001 mm. in a 2-cm. cylindrical tube.

Effect of Pressure on γ.

The range of pressures which could be used with the experimental method described above was rather restricted, since the pressure of the phosphine had to be of such a magnitude that there was complete absorption of the zinc lines at 210 mμ. The following method, however, allows of the calculation of quantum yields down to very low pressures.

Table IV contains the record of a series of experiments using different pressures of phosphine with the same time of exposure and intensity of spark.

Table IV.—Room temperature 15° C., 2 cm. cylindrical tube.

p_{PH_3} (mm.).	Rate (mm./min.).	Calculated rate.
760	0·0022	—
44	0·0022	—
5	0·0011	—
0·226	0·00033	0·00057
0·072	0·00012	0·00020
0·0365	0·000065	0·00008

The quantum yield is independent of pressure between 44 and 760 mm. If the reduction in rate below 44 mm. pressure is owing wholly to incomplete absorption, then the variation in rate with pressure is simply expressed by the equation

$$R = R_\infty (1 - e^{-kp}),$$

where R_∞ is the rate when absorption is complete, R that at pressure p mm. and k is a constant depending only on the dimensions and shape of the insolation tube and the extinction coefficient of phosphine for the wave-lengths in the region of 210 mμ. k was obtained from the experiment at 5 mm. using R_∞ from the experiments at 44 and 760 mm. and assuming that the quantum yield at 5 mm. is the same as that at 44 mm. The third column of Table IV was calculated from this value of k. The agreement is reasonably good in view of the exponential factor governing R; however, it is sufficient to show that the quantum yield is independent of pressure from 0·04 to 760 mm.

Effect of Temperature on γ.

Preliminary experiments were made to find when thermal dissociation becomes appreciable with this type of apparatus. At 340° C., the phosphine

pressure being 40 mm., 0·0315 mm. of hydrogen were produced in 30 minutes, at 290°, 0·0015 mm. Photochemical experiments were therefore impossible at temperaures much above 300° as the photo-reaction yielded about 0·05 mm. hydrogen in 10 minutes.

In order to reduce pressure readings at high temperatures to 15° C., hydrogen was admitted to the McLeod gauge and R_1 to a pressure of 0·05 mm. R_1 was then heated up to 300° C., pressure readings being taken at suitable temperature intervals. At pressures of the order of 0·05 mm. of hydrogen, thermal effusion is appreciable so that the reduction of the pressure readings by calculation is difficult to carry out accurately.

In these experiments phosphine was used as the photometric gas in R_2. Owing to deposition of red phosphorus on the lens of R_2, calibration experiments were made at the beginning and end of each run. Table V gives two series of experiments, where it is seen that the quantum yield is practically independent of temperature.

Table V.—Pressure of PH_3, 40 mm. 7 cm. bulb. Zn spark.

p_{H_2} in R_1 (mm.)	p_{H_2} in R_2 (mm.)	Temperature (° C.)	p_{H_2} in R_1 reduced to 15°.	γ rel. to 15° C.
0·0165	0·0430	25	0·0162	1·0
0·0283	0·0273	267	0·0232	1·1
0·0300	0·0351	212	0·0254	0·9
0·0197	0·0220	176	0·0171	0·9
0·0131	0·0167	117	0·0118	0·8
0·0178	0·0161	73	0·0166	1·0
0·0145	0·0131	30	0·0141	1·0
0·0270	0·0215	25	0·0265	1·0
0·0457	0·0191	324	0·0364	1·5
0·0425	0·0244	232	0·0361	1·1
0·0255	0·0173	208	0·0215	0·9
0·0390	0·0220	140	0·0345	1·1
0·0363	0·0208	90	0·0333	1·1
0·0257	0·0173	33	0·0250	1·0

Discussion of Reaction Mechanism.

The experiments described above corroborate those using excited mercury atoms for dissociation of the phosphine molecule, in those cases where comparison can be made. The effect of atomic hydrogen may be mentioned again, as the experimental data in I provide direct proof that the photochemical decomposition is inhibited by hydrogen atoms. The low quantum yield, in this case also, is probably owing to recombination of PH_2 and H on the walls.

It is rather surprising to find that temperature has no appreciable influence on γ. This means that temperatures up to 300° C. do not alter the relative probabilities of the reactions $PH_2 + PH_2 = P_2 + 2H_2$, $H + H = H_2$ and $PH_2 + H = PH_3$. If these reactions require only small energies of activation the result is to be expected. Unfortunately, experiments could not be extended to 400–500° C. where adsorption of molecular hydrogen begins on silica surfaces.* At these temperatures the altered surface might well exert a large influence on the secondary reactions.

At high phosphine pressures, there is the possibility that the secondary reactions postulated above may go through the medium of ternary collisions. It is therefore of importance, first of all, to calculate the stationary concentration of hydrogen atoms, and then find if a hydrogen atom can collide with another of its kind and a third molecule before reaching the wall of the reaction tube. When the concentration of hydrogen atoms is stationary,

$$-\frac{d[H]}{dt} = \frac{1}{T}[H],$$

where T is the time required for a hydrogen atom to diffuse to the walls, assuming that this is the only way in which hydrogen atoms are removed from the gas. $d[H]/dt$ may easily be obtained from the experimental data and amounts to about 10^{-5} mm. per second. T may be obtained from the diffusion coefficient (D) of hydrogen atoms through phosphine by means of the Einstein equation $r^2 = 2DT$, r being the radius of R_1. Taking the radius of the hydrogen atom as $0{\cdot}5 \times 10^{-8}$ cm., D, on calculating from the Stefan-Maxwell equation $D = \kappa/\sigma_{12}^2 (1/M_1 + 1/M_2)^{\frac{1}{2}}$, amounts to 1·1 for phosphine at 760 mm. T is therefore 10 seconds and $[H] = 10^{-4}$ mm. Now one hydrogen atom makes about 10^{10} collisions per second with phosphine molecules at 760 mm.; it will therefore make 10^3 collisions per second with hydrogen atoms. If a phosphine molecule is also involved in the collision between the two hydrogen atoms, there will be between 1 and 10 ternary collisions before the hydrogen atom reaches the walls, if the ratio of the number of bimolecular collisions to that of ternary collisions is as the diameter of the hydrogen atom to its mean free path in phosphine.

The hydrogen atom takes 10 seconds to reach the walls if it is generated in the middle of the bulb. At 760 mm., however, absorption of light at 210 mμ is practically complete in a layer less than 1 cm. in thickness, so that the time required for the atom to reach the walls is more nearly 1 second instead of 10

* Bone and Wheeler, ' Phil. Trans.,' A, vol. 206, p. 1 (1906).

seconds. Hence there is slight balance in favour of the hydrogen atom (or the PH_2 radical) reaching the walls rather than making a ternary collision. At pressures less than 760 mm. collisions with the walls are very much more probable. It may be concluded that, in the experiments described above, the secondary reactions in the photochemical decomposition of phosphine take place mainly on the walls of the reaction tube, thus explaining the negligible influence of pressure on the quantum yield. It would be interesting to know, if the concentration of hydrogen atoms and PH_2 radical were increased by adding inert gas to a pressure of several atmospheres and/or increasing the intensity of the incident radiation, whether the ternary collisions, which would take place under these conditions, would have any effect on the quantum yield.

Having now obtained quantum yields of the direct reaction and also the relative efficiency of the photo-sensitized decomposition of NH_3 and of PH_3, an estimate may be made of the square of the effective collision radii (σ_P^2) of the PH_3 molecule and the $2\,^3P_1$ mercury atom. This estimate is based on the assumption that the secondary reactions in the direct and photo-sensitized reactions are identical. Such an assumption has been substantiated for ammonia (see I) and is probably true for phosphine. σ_P^2 is given by the equation

$$\frac{R_{NH_3}}{R_{PH_3}} = \frac{\gamma_{NH_3}}{\gamma_{PH_3}} \frac{\sigma_N^2}{\sigma_P^2} \frac{(1/M_{Hg} + 1/M_{NH_3})^{\frac{1}{2}}}{(1/M_{Hg} + 1/M_{PH_3})^{\frac{1}{2}}}.$$

In the 2 cm. tube $R_{NH_3}/R_{PH_3} = 0{\cdot}073$, $\gamma_{NH_3} = 0{\cdot}25$, $\gamma_{PH_3} = 0{\cdot}49$, $\sigma_N^2 = 2{\cdot}94 \times 10^{-16}$ cm.^{2},* so that the value of σ_P^2 is $27{\cdot}5 \times 10^{-16}$ cm.^{2}

No data for the quenching of resonance radiation by PH_3 are yet available. If subsequent experiment gave σ_P^2 of the order $27{\cdot}5 \times 10^{-16}$ cm.^{2}, then it may be concluded that every collision involving deactivation of the mercury atom results in dissociation of the phosphine molecule. According to the calculations in I, this appears to be the case for ammonia, so that it would be of importance to find whether phosphine behaves in the same way.

It has been pointed out by Zemanski* and by Bates† that those simple molecules which possess large quenching radii have a vibration band in which the energy associated with the quantum corresponds closely to the difference in energy between the $2\,^3P_1$ and $2\,^3P_0$ states of the mercury atom, which amounts to 0·218 volts. For example, CO_2 has a σ^2 of $2{\cdot}48 \times 10^{-16}$ cm.^{2},

* Zemanski, 'Phys. Rev.,' vol. 36, pp. 919, 930 (1930).

† 'J. Amer. Chem. Soc.,' vol. 54, p. 569 (1932).

the nearest vibration band being at 0·253 volts; while for NO, $\sigma^2 = 24 \cdot 7 \times 10^{-}$ cm.^{2} and a band at 0·235 volts. Although σ^2 for PH_3 is of the same magnitud as that for NO, there is no vibration band close to 0·218 volt, the nearest ban at 4·2 μ* corresponding to 0·29 volts. The exchange of energy betwee Hg $2\,^3P_1$ and PH_3 cannot, therefore, resemble the process suggested b Zemanski.

The mechanism of the photochemical decomposition of phosphine, so far a it is revealed by these experiments and calculations, may be summarized a follows: PH_3 is dissociated into PH_2 and H, which diffuse to the walls. Thes radicals undergo secondary reactions at the walls such that the net quantum yield is about 0·5 in a 2-cm. tube. The three main secondary reactions would appear to be $PH_2 + PH_2 = P_2$ (red phosphorus) $+ 2H_2$, $H + H = H_2$, $PH_2 + H = PH_3$. The reaction $PH_2 + H$ is slightly favoured by increase of surface and by an increase in the number of hydrogen atoms adsorbed on the walls. Temperatures up to 300° C. have little effect, so that the heats of activations of the surface reactions are probably small.

Part IV.

The Photochemical Oxidation of Phosphine.

It has been shown in II that oxygen strongly accelerates the photo-sensitized decomposition of phosphine, while the subsequent addition of argon still further increases the rate of oxidation. The latter influence of argon is indicative of the intervention of a chain mechanism. Quantitative experiments are, however, not easy with the photo-sensitized reaction, as it is difficult to estimate the extent of the deactivation of the mercury atoms by oxygen and by argon. With the direct photochemical reaction, conditions are rather simpler, so that it is possible to make more detailed calculations and finally to obtain quantum yields of the oxidation process, so that the length of the reaction chains may be calculated.

The experimental procedure was as follows: R_1 was filled with PH_3, the pressure being about 0·05 mm. With the ammonia photometer (R_2) in use an exposure was made in order to measure the rate of decomposition of the PH_3. R_1 was again filled with phosphine to the same pressure, the PH_3 was condensed out with liquid air and then oxygen added (about 0·05 mm.). The PH_3 was evaporated and the mixture illuminated, R_2 measuring the

* Robertson and Fox, 'Proc. Roy. Soc.,' A, vol. 120, p. 128 (1928).

intensity of the spark as before. After condensing out the residual PH_3 into a liquid air trap provided with a tap (having a volume of about 10 c.c. compared with 600 c.c. of R_1 + McLeod) the pressure of residual gas was measured. The tap on the liquid air trap was then closed, the non-condensable gases pumped off and the pressure of the remaining phosphine determined. From these measurements, which are given in Table VI, after making a small correction for pumping off a little phosphine with the non-condensable gas, the amount of PH_3 decomposed was easily calculated.

Table VI.—Temperature 18° ± 1° C. Zn spark. 7 cm. bulb.

p_{PH_3} initial.	p_{O_2} added.	$p$uncond. +0·0085 mm.	p_{PH_3} residual.	p_{PH_3} decomposed.	$p_{H_2+N_2}$ in R_2.	Chain length observed.	Chain length calculated.
0·0970	—	0·0103	—	0·0014	0·0232	—	—
0·0900	0·0670	0·0585	0·0505	0·0365	0·0226	265	1100
0·1235	—	0·0113	—	0·0021	0·0214	—	—
0·1210	0·0600	0·0545	0·0635	0·0490	0·0179	240	1310
0·1235	0·1055	0·1055	0·0610	0·0545	0·0116	270	2350
0·0715	—	0·0093	—	0·0006	0·0217	—	—
0·0685	0·0570	0·0450	0·0200	0·0400	0·0113	1150	663
0·0650	0·0955	0·1040	0·0255	0·0310	0·0086	550	1110
0·0705	—	0·0197	—	0·0084	0·0480	—	—
0·0645	0·0165	0·0305	0·0315	0·0245	0·0232	—	—
0·0705	0·0535	0·0520	0·0170	0·0450	0·0191	180	818
0·0695	0·0805	0·0775	0·0120	0·0490	0·0161	190	1010
0·1035	—	0·0217	—	0·0100	0·0440	—	—
0·1020	0·0155	0·0315	0·0675	0·0260	0·0155	—	—
0·1025	0·0560	0·0575	0·0445	0·0495	0·0173	59	1030
0·0995	0·0820	0·0765	0·0265	0·0645	0·0155	190	1480
0·0510	—	0·0153	—	0·0050	0·0410	—	—
0·0515	0·0540	0·0530	0·0083	0·0347	0·0179	250	500
0·0520	0·0790	0·0785	0·0055	0·0380	0·0167	205	740
0·0570	—	0·0135	—	0·0038	0·0393	—	—
0·0550	0·0435	0·0360	0·0167	0·0297	0·0107	215	430
0·0605	0·0570	0·0495	0·0220	0·0300	0·0071	265	620
0·0605	0·0770	0·0780	0·0215	0·0305	0·0095	160	840

0·0085 mm. is the vapour pressure of the PH_3.

After the third set of experiments R_1 was taken down and cleaned.

In the penultimate column of the table the results are multiplied by $1/\gamma$ since the quantum yield in the 7 cm. tube is less than unity.

The third column in Table VI shows that the pressure of non-condensable gas is approximately equal to the initial pressure of oxygen although the amount of phosphine decomposed is quite large. The same observation was

made during the experiments on the photo-sensitized oxidation. In the present case also, it would appear that the main oxidation reaction is $PH_3 + O_2 = H_2 + HPO_2$, the HPO_2 being deposited on the walls. All subsequent calculations about chain lengths will therefore be based on the assumption that this reaction takes place according to this equation.

In suggesting a mechanism for the reaction it will be supposed that the phosphine molecule is decomposed according to the equation $PH_3 + h\nu = PH_2 + H$. The PH_2 radical reacts on colliding with the first oxygen molecule it encounters. During this collision some molecule or radical is produced which is able, by virtue of its energy content or chemical unsaturation, to initiate a chain reaction between PH_3 and O_2. At 0·1 mm. of PH_3 according to the estimates made on p. 550, the hydrogen atom could make 10^6 collisions per second with O_2 molecules. As the H atoms would diffuse to the wall in about 10^{-4} seconds, the formation of excited H_2O or of OH by the ternary collision $H + H_2 + O_2 = H_2O + H$ is improbable, so that the possibility of H_2O or OH starting a chain may be excluded.

It has been shown that with small pressures of phosphine the rate of the photochemical decomposition is proportional to the pressure so that

$$-\frac{d[PH_3]}{dt} = kI^1[PH_3], \tag{1}$$

and for the photo-oxidation

$$-\frac{d[PH_3]}{dt} = kIK[PH_3]^2[O_2]\{1 + \mu[H_2]/([PH_3] + [O_2])\}, \tag{2}$$

where k is a constant, I and I^1 are the intensities of the incident radiation. K is another constant depending on the chain characteristics of the oxidation. The factor including H_2 represents the inert gas effect, μ being a constant.

If a and b are the initial concentrations of PH_3 and O_2 respectively and x the concentration of PH_3 decomposed, then from (1)

$$\frac{dx}{dt} = kI^1(a - x)$$

or

$$kI^1t^1 = ln\frac{a}{a - x} \tag{3}$$

where t is the time of illumination. Now Table VI shows that the amount of PH_3 decomposed is nearly equivalent to the amount of O_2 used up and to the amount of hydrogen formed so that (2) becomes

$$\frac{dx}{dt} = kIK(a - x)^2(b - x)\{1 + \mu x/(a + b - 2x)\}. \tag{4}$$

The integration of (4) is considerably simplified for it is probable that μ is of the order of 0·1* so that the inert gas factor may, to a first approximation, be neglected. Upon integrating the simplified form of equation (4)

$$kIt \,.\, \mathrm{K} = \frac{1}{a\,(b-a)}\,\frac{x}{a-x} + \frac{1}{(b-a)^2}\,ln\,\frac{b\,(a-x)}{a\,(b-x)}. \qquad (5)$$

If the chain is unbranched, the chain length ν is given by

$$\nu = \mathrm{K}\,[PH_3]\,[O_2]. \qquad (6)$$

From the experiments on the photo-dissociation and the readings of the photometer $lna/(a-x)$ and It and therefore k can be calculated. Similarly the experiments on the photo-oxidation yield the value of $k\,.\,\mathrm{K}$ by means of (5). Hence K is obtained and from (6) the chain length.

The number of links ν^1 in a straight chain assuming reaction at every collision is given by the formula†

$$\nu^1 = \frac{ab}{(a+b)^2}\cdot\frac{1{\cdot}5\,d^2}{\lambda^2},$$

where d is the average distance a chain diffuses to the walls where it is supposed to be broken. λ is the mean free path of the chain in centimetres at pressure $(a+b)$. In the present case λ is difficult to estimate, since the nature of the chain carriers is not known, but at 0·1 mm. pressure $\lambda = 10^{-1}$ cm. is not an unreasonable estimate. If $a = b = 0{\cdot}05$ mm. and $d = 3{\cdot}5$ cm., $\nu^1 = 450$. Using this value the last column of Table VI has been constructed.

The calculated and observed values of ν are of the same order of magnitude, although the calculated results are higher consistently by a factor of 2 — 5. The simplest interpretation of this approximate agreement would be that the chains are straight, reaction occurring at every collision of the chain carrier with O_2 or with PH_3, according to the nature of the carrier, and that every chain which reaches the wall terminates there. The low value of the observed chain length is probably due to deactivation in the gas phase—a phenomenon which becomes very marked at higher pressures (*cf.* Dalton and Hinshelwood, *loc. cit.*).

Phosphine and oxygen mixtures are, however, spontaneously inflammable if the pressure is raised to a sufficient degree. The chain theory interprets this as an indication of branched chains. Suppose, therefore, that the phosphine

* Melville, 'Trans. Faraday Soc.,' vol. 28, p. 814 (1932).

† Semenoff, 'Z. Physik,' vol. 46, p. 109 (1927); Dalton and Hinshelwood, 'Proc. Roy. Soc.,' A, vol. 125, p. 294 (1929).

oxygen chain branches at every cycle. Let n be the average length of any chain from the starting point to the end of the branch, then ν the total number of molecules of PH_3 decomposed per initial chain centre (which is the length of a straight chain) is given by

$$\nu = 1 + (2 + 2^2 + 2^3 + \ldots \text{ to } n \text{ terms})$$
$$= 1 + 2^{n+1} - 2.$$

From Table VI $\nu \doteqdot 200$, so that $n = 7$. Therefore if branching does occur at every cycle, the chain is so short that it will not reach the wall. But as an increase in the diameter of the reaction tube increases the chain length, the chains must reach the wall and therefore the probability of branching must be less than 1 in 200.

If the agreement between calculated and observed chain lengths obtained in Table VI is regarded as purely fortuitous, and if the chains are reflected from the wall, then the probability of branching must be even smaller than 5×10^{-3}. That the condition of the walls does alter the probability of termination has been demonstrated,* but the effect is less than an order of magnitude, and thus does not alter the significance of the above discussion to any great extent. In order to settle the matter unequivocally, experiments would require to be devised in which the probability of branching and the probability of termination could be separately determined.

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Summary.

The absorption spectrum of phosphine has been photographed at room temperature. It consists of a region of continuous absorption beginning at 230 mμ, which is preceded by four weak diffuse bands. At 300° C. the bands disappear and the limit moves towards the longer wave-lengths.

The photo decomposition of phosphine by light from zinc and aluminium sparks has been studied. The reaction is $4PH_3 = P_4 + 6H_2$, the phosphorus being deposited as the red variety. The quantum yield (γ) is 0·56 in a 7 cm.

* Hinshelwood and Clusius, 'Proc. Roy. Soc.,' A, vol. 129, p. 589 (1930); also Part II of this investigation.

bulb, falling to 0·49 in a 2 cm. cylindrical tube. Temperatures up to 300° C. do not influence γ. Molecular hydrogen has no effect, but atomic hydrogen decreases γ. The mechanism of the reaction is discussed and compared with the photo-sensitized reaction.

On adding oxygen to PH_3 and illuminating, a stable chain reaction occurs, and with pressures of $PH_3 = O_2 = 0{\cdot}05$ mm. $\gamma = 200$. The significance of the value is discussed in relation to the theory of branched chains. It is concluded that the probability of branching at any one cycle is not more efficient than 5×10^{-3}.

A compact and sensitive form of combined reaction tube and McLeod gauge is described.

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AN INTENSITY FILTER FOR THE MERCURY LINE AT 253·7 mμ.

By H. W. Melville and H. J. Walls.

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In photochemical chain reactions, the effect of the variation of the intensity of the incident radiation provides important information about the termination of the chains. If the rate of reaction is proportional to the first power of the intensity, it may be concluded that the chain carrier is destroyed in a bimolecular collision with another molecule or by a collision with the walls of the reaction tube. On the other hand, if the rate is proportional to the square root of the intensity, the chains are terminated by self-destruction, *e.g.*, by the combination of two atoms. Examples of these types of behaviour may be seen in the recent series of papers on the hydrogen-chlorine reaction by Ritchie and Norrish.[1] This differentiation in the mechanism of chain termination has now gained added importance, for it is believed that the position of the upper and the lower limits for explosion of thermal chain reactions is determined respectively by gas phase and by wall destruction of the carriers. Photochemical experiments on the intensity relationships outside these limits should be able, therefore, to give confirmation of the hypotheses which have been advanced to explain these phenomena.

No great difficulty occurs in measuring the variation in intensity when a thermopile or photoelectric cell is employed and the reaction vessel is at room temperature. If, however, the reaction bulb is in a furnace and the source of light is of considerable area, such as a mercury lamp, the difficulties are increased. Some means are, therefore, required to vary the intensity by a known and easily controllable amount. The rotating sector is not suitable for this type of work, as it really alters the duration of exposure and not the intensity.[2] In addition, matters are rendered more complicated by the possible existence of induction periods and photochemical after effects. Wire gauze screens, especially if constructed of round wire, are not, in general, reliable as it is difficult to calculate exactly how much light is cut off. There remains then some type of filter partly transparent to the radiation being used.

This paper is concerned with a liquid filter for use with the mercury resonance line at 253·7 mμ and hence is specially suitable for mercury sensitised reactions. In order to vary the transmission of a liquid filter, a solution is most convenient to use as only a single cell is required. The solution must, however, have the following properties if it is to be reliable (*a*) stability to light of 253·7 mμ, (*b*) components to be easily obtained in a pure state, (*c*) normal behaviour of the components so that Beer's law is obeyed exactly, (*d*) rapidity and ease of preparation.

These criteria are fulfilled by mixtures of carbon tetrachloride and *n*-hexane or cyclo-hexane. Ordinary sulphur free carbon tetrachloride is suitable, but the hexane or cyclo-hexane must be specially purified

[1] *Proc. Roy. Soc.*, **140A**, 99, 112, 713, 1933.
[2] Griffith and McKeown, *Photochemical Processes*, p. 664.

in order that its absorption at 253·7 mμ may be negligible. The hexane and cyclo-hexane purified for spectroscopic work, as supplied by British Drug Houses, were used in the present instance and found to be entirely satisfactory. The rapid rise in the extinction coefficient of carbon tetra-chloride to light of 253·7 mμ cuts out all light from the mercury arc which might be absorbed by the reactants directly. One advantage of using cyclo-hexane in preference to *n*-hexane is that its boiling-point is close to that of carbon tetrachloride and therefore any loss of the solution by evaporation, *e.g.*, when placed in the proximity of a furnace, does not lead to any disturbing change in concentration.

Experimental.

A 5 mm. absorption cell was employed for the photochemical experiments. A series of solutions was therefore made up to cut off from 20 per cent. to 80 per cent. of the light as measured approximately by the photochemical reaction. The extinction coefficients of the solutions were then

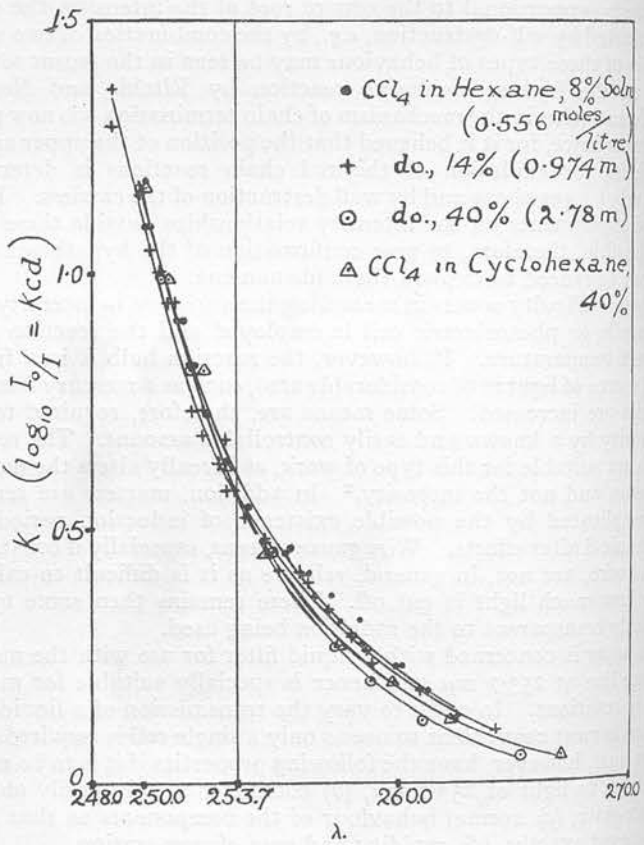

FIG. 1.

measured exactly by means of a Bellingham and Stanley rotating sector photometer used in conjunction with a Bellingham and Stanley quartz spectrograph, giving the spectrum from about 210 to 800 mμ on a 10 in. plate. An iron spark was employed as source of light. The wave-lengths

for the positions of equal blackening on the plate were determined by comparison with an enlarged calibrated photograph of the iron spark spectrum, the plates being examined with the aid of a lens. The positions were determined at least twice in each plate, with an interval in between, in order to eliminate possible errors due to fatigue. The wave-lengths could easily be determined to within 0·2 mμ in this way.

The extinction coefficient — wave-length curves for four solutions are shown in Fig. 1. The value of the extinction coefficient used is defined by the equation

$$\log_{10} I_0/I = kcd \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is the extinction coefficient, d the thickness of the layer in cm., and c the concentration in moles per litre. It will be seen that the curves for three different concentrations (0·56, 0·97, 2·78 moles per litre) fall practically together ; the difference in the ordinates may be put down to experimental error. This means that Beer's law is obeyed exactly within this region of concentration. The two solutions of equal concentration in hexane and in cyclohexane also show identical absorption in this region.

The values of k at 253·7 mμ as measured off a large scale graph are :—

0·56	moles per	litre	0·598
0·97	,,	,,	0·575
2·78	,,	,,	0·590
	Average	.	0·588

Using this value of k, the percentage transmission for any concentration and layer thickness, or alternatively the concentration and/or layer thickness necessary to cut off a given amount of radiation at 253·7 mμ, can be rapidly calculated by means of equation 1.

To test the stability of the filter, a solution of concentration 2·78 moles per litre made up with hexane was exposed to a mercury lamp with a cool cathode running at 5 amps. and 40 volts for four hours. Some change occurred, for the liquid evolved some hydrochloric acid and it was found that the extinction coefficient at 253·7 mμ had increased by about 20 per cent. A similar result was obtained with cyclohexane. A filter was therefore not employed for much longer than fifteen minutes. As the quantity of solution required to fill the quartz cell only amounted to a few c.c., this procedure was not unduly extravagant in the use of the comparatively expensive hexane.

In the Tables below are given data of a few experiments on the mercury sensitised reaction between hydrogen and nitrous oxide. The investigation[3] of the thermal reaction had shown that it was of the chain type,

TABLE I.—Low Press. 5 cm. Reaction Bulb. Temp. 580° C. 1 : 1 Mixture. Total Press. 16·00 mm.

Composition of Filter.	Rate Rel. to Hexane (R).	Intensity Rel. to Hexane (I).	R/I.
n-hexane . . .	1·00	1·00	1·00
1·2 c.c. in 25 c.c. solution	0·86	0·80	1·07
2·0 ,, ,, ,,	0·70	0·68	1·03
2·0 ,, ,, ,,	0·73	0·68	1·07
3·5 ,, ,, ,,	0·53	0·51	1·04
10·0 ,, ,, ,,	0·183	0·15	1·20

The absolute rate of reaction with pure hexane was 0·82 mm. of water per min.

[3] Melville, *Proc. Roy. Soc.*, in the press.

TABLE II.—High Press. Temp. 510° C. 1 : 1 Mixture. Press., 100 mm.

Composition of Filter.	Rate Rel. to Hexane (R).	Intensity Rel. to Hexane (I).	R/I.	$R^{\frac{1}{2}}/I$.
n-hexane . . .	1·00	1·00	1·00	1·00
2 c.c. CCl_4 in 25 c.c solution	0·80	0·68	1·17	0·94
3·5 ,, ,, ,,	0·67	0·51	1·31	0·87
5·0 ,, ,, ,,	0·49	0·38	1·29	0·64

The absolute rate of reaction with pure hexane was 0·80 mm. water per min.

initiated by the dissociation of a nitrous molecule into N_2 and O, follow by the reaction $O + H_2 \rightarrow OH + H$. The chain is probably propagate by the reactions

$$OH + H_2 \rightarrow H_2O + H$$
$$H + N_2O \rightarrow OH + N_2.$$

Further, there was indirect evidence that the chains were terminat principally in the gas phase by self-neutralisation at pressures of the orde of 100 mm., whereas at 10 mm., wall deactivation was most importan It would be expected then that in the photochemical experiments, (a)

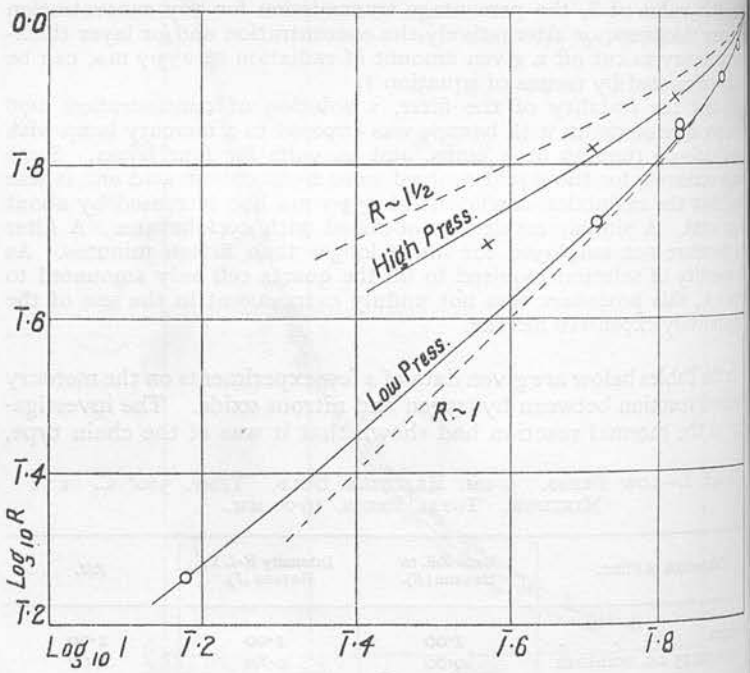

Fig. 2.

high pressures the rate should be proportional to the square root of the intensity, and (*b*) at low pressures, a linear relation should hold between rate and intensity.

Full details are not given of the experiments (they will be published later) as the results quoted are solely for the purpose of indicating the

usefulness of the filter in providing independent confirmation of the mechanism of the termination of the chains.

In Table I., it will be observed that the rate (R) is very nearly proportional to the intensity (I) as is indicated by the constancy of the quantity R/I. At high pressures R/I is no longer constant and neither is R^2/I so that the rate must be proportional to a power of the intensity between 0·5 and 1·0. Even at 100 mm., however, wall termination was quite noticeable and the latter result is to be expected. The dark reactions were negligible in both cases; the chain length was of the order 10^3.

In Fig. 2, $\log_{10} R$ has been plotted against $\log_{10} I$ using the results in Tables I. and II., and it will be observed that the high pressure experiments lie fairly close to a line having a slope of 0·5, whereas the low pressure experiments conform nearly to a line of unit slope.

Summary.

A liquid filter is described for altering the intensity of the 253·7 mμ line from a mercury arc lamp. The absorbing liquid is sulphur free carbon tetrachloride which is mixed with *n*-hexane or cyclohexane. The extinction coefficients of a number of solutions were determined and found to obey Beer's law. The applicability of the filter is shown by experiments on the photochemical chain reaction between hydrogen and nitrous oxide at high and at low pressures where the rate is respectively proportional to the square root and to the first power of the intensity.

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The Kinetics of the Reaction between Hydrogen and Nitrous Oxide.—I.

BY H. W. MELVILLE.

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The Kinetics of the Reaction between Hydrogen and Nitrous Oxide.—I.

By H. W. MELVILLE.

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Until about five years ago, the theoretical treatment of the mechanism of the oxidation of simple molecules had been comparatively neglected. Prior to this, however, considerable progress had been made in the study of the kinetics of thermal and photochemical gas reactions. That knowledge has now been successfully applied and extended to solve some of the major problems in combustion chemistry, and thereby has given rise to the development of the theory of thermal chain reactions. Hitherto, the investigation of these reactions has been confined almost entirely to oxidations by molecular oxygen.* It is known,† however, that many gases ignite in nitrous oxide at about the

* Exceptions are the Cl_2, Br_2 and HBr sensitized decomposition of O_3; Bodenstein, Padelt and Schumacher, 'Z. phys. Chem.,' B, vol. 5, p. 209 (1929); Lewis and Feitknecht, 'J. Amer. Chem. Soc.,' vol. 53, p. 2910, p. 3565 (1931).

† Dixon and Higgins, 'Proc. Manc. Phil. Soc.,' vol. 71, p. 17 (1927).

same temperature as they do in oxygen, and it might be anticipated that here too, a chain process is in operation. The object of studying the interaction of hydrogen and nitrous oxide was to determine whether it is a chain reaction, and if so, to make a detailed analysis of its mechanism by the kinetic method.

One of the first criteria in looking for the possibility of the propagation of chains in a gaseous mixture is that the reaction must be exothermic. This condition is amply fulfilled in the present instance, for 75 k.cal. are liberated per mole of water formed. Indeed, the reaction is even more exothermic than the formation of one mole of water from hydrogen and oxygen, when only 50 k.cal. are evolved. This greater exothermicity is due to the fact that 45 k.cal. are required to dissociate 1 mole of N_2O into N_2 and O, whereas the production of 1 mole of O atoms from O_2 requires about 60 k.cal.

There was another important reason for choosing N_2O as one of the participants in the reaction. Recently, the kinetics of the decomposition have been very thoroughly worked out,* and it is now thought probable that the first step in the thermal decomposition is the formation of a nitrogen molecule and an oxygen atom from an excited molecule, the necessary energy of activation being derived from a collision between molecules of a sufficiently high energy content. In addition, experiments have shown what effect inert gases exert on the rate of production of these activated molecules.

Several other interesting points arise out of the use of the N_2O molecule, for example, there is only one oxygen atom available and the nitrogen molecule may, in suitable circumstances, play the part of an energy scavenger. Hydrogen was chosen as the other reactant for the reason that since the kinetics of the H_2–O_2 reaction have been worked out in some detail, they might prove helpful in elucidating the mechanism of the H_2–N_2O reaction. It is hoped, however, to extend the experiments to the reactions of other simple molecules with nitrous oxide.

The H_2–N_2O reaction has been studied on the surface of a platinum filament by Cassel and Gluckauf† at low pressures and with an excess of hydrogen, under these conditions there is a complete change in the mechanism as the temperature of the catalyst is increased beyond 775° C. Similarly Hinshelwood‡ found at high pressures that the kinetics of the reaction differed depend-

* Volmer and Kummerow, 'Z. phys. Chem.,' B, vol. 9, p. 141 (1930); Nagasako and Volmer, *ibid.*, vol. 10, p. 414 (1930), vol. 11, p. 420 (1931); Volmer and Froelich, *ibid.*, vol. 19, pp. 85, 89 (1932); Musgrave and Hinshelwood, 'Proc. Roy. Soc.,' A, vol. 135, p. 23 (1932); *ibid.*, vol. 137, p. 25 (1932).

† 'Z. phys. Chem.,' B, vol. 19, p. 47 (1932).

‡ 'Proc. Roy. Soc.,' A, vol. 106, p. 292 (1924).

ing upon whether the N_2O or the H_2 were in excess. The possible bearing of these observations on the results to be described below will be discussed later.

When hydrogen was sealed up with nitrous oxide at about atmospheric pressure in a Jena glass bulb, Hinshelwood* noticed that the rate of formation of water was no faster than the rate of decomposition of nitrous oxide at about 700° C. It was suggested that the first stage in the reaction was the decomposition of nitrous oxide into nitrogen and oxygen molecules, the oxygen thereafter being quickly removed by combination with hydrogen, since the H_2-O_2 reaction is very rapid at this temperature. The net rate is determined by the slowest process, namely, the decomposition of the nitrous oxide. It is to be observed, however, that at the lower temperatures used in these experiments, the rate of H_2O formation was somewhat faster than that of the decomposition of N_2O.

In sharp disagreement with these experiments are the results of Dixon and Higgins (*loc. cit.*), who found that a jet of hydrogen inflamed spontaneously in an atmosphere of nitrous oxide at about 550° C., or 150° below the temperature of Hinshelwood's experiments, where the rate of decomposition of N_2O is very small. The temperature of ignition depended on pressure and was preceded by an induction period. In this latter dynamic method the composition of the mixture could, of course, vary within wide limits. It is one of the objects of this paper to determine, if possible, the reason for this discrepancy.

The question of the mechanism of this reaction can be most logically approached by considering the possible ways in which it might occur :—

(1) Heterogeneous reaction, exclusively on the walls of the reaction tube.
(2) Homogeneous bimolecular reaction, $H_2 + N_2O \rightarrow H_2O + N_2$.
(3) Decomposition of N_2O followed by rapid oxidation of H_2, *i.e.*,

$$N_2O + N_2O = 2N_2 + O_2.$$
$$2H_2 + O_2 = 2H_2O.$$

(4) Chain reaction : various mechanisms.

While the possible types of reaction have been separately classed above, the chain process may include 1, 2 and 3 since (*a*) initiation of the chain may be homogeneous or heterogeneous, (*b*) similarly, termination may occur in the gas or at the walls, and (*c*) propagation probably involves a series of bimolecular encounters.

* 'Proc. Roy. Soc.,' A, vol. 106, p. 292 (1924).

The first point to be settled about this reaction is, therefore, the class to which it belongs; the second, by extending the experiments in suitable directions, to determine, as far as the present method will allow, the nature of the individual processes leading to the final products, which appear to be mainly N_2 and H_2O.

Experimental.

Consideration of the equation $H_2 + N_2O = N_2 + H_2O$ shows at once that there is no pressure change during reaction, and therefore it would appear that the convenient and sensitive manometric method could not be employed for measuring the velocity. By withdrawal of the water by absorption with P_2O_5 or $CaCl_2$, the resultant decrease in pressure may be used as a measure of the extent of reaction.

The apparatus consisted of a silica reaction bulb placed in an electric furnace. The bulb was provided with a wide neck (1·7 cm. diameter) and a silica-glass ground joint so that a porcelain boat containing P_2O_5 or $CaCl_2$ could be inserted in the neck just outside the mouth of the furnace. The volume of the "cold" parts of the reaction bulb system was reduced to less than 5% of the total by packing with glass beads. In order to ensure rapid and thorough mixing of

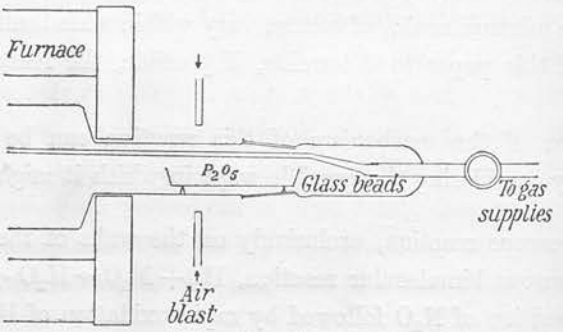


FIG. 1.

the reactants, the gases were lead from the reservoirs directly into the middle of the bulb by a silica tube 3 mm. in diameter as is shown in fig. 1. Neglect of these precautions led to the variation of the kinetics with the order of addition of the gases to the reaction tube owing to the time required for interdiffusion. Such a variation was exaggerated to some extent for, as will be seen below, the rate of reaction is nearly independent of the concentration of hydrogen and directly dependent on that of nitrous oxide. In some bulbs there was fused to the neck a wide side tube which could be immersed in a CO_2/ether bath at $-80°$ C. The bulb was connected to a mercury condensation pump for

evacuation and to a number of gas reservoirs. A capillary mercury manometer served as a pressure gauge. The temperature of the furnace was manually controlled to within 1° C. in the range 500°–800° C., using a Pt/Pt-Rh thermocouple and millivoltmeter. Nitrous oxide was obtained from a cylinder and contained not more than 0·2% air. This gas was first dried by slow passage over P_2O_5, then collected in a liquid air trap and fractionated. The hydrogen was electrolytic and was freed from traces of oxygen by palladized asbestos and dried with P_2O_5. Argon and nitrogen were freed from traces of oxygen by passing over a tungsten filament at 2000° C.

The absorbing agent has to be situated just outside the furnace and therefore the water vapour requires a short time to diffuse to the $CaCl_2$. Such a time lag between production and removal leads to the establishment of a " stationary " concentration of water vapour in the reaction tube.

The first problem to be solved was the determination of this stationary concentration, and the second, to find if the variation in p_{H_2O}, as must inevitably occur during the progress of the reaction, had any measurable effect on the kinetics. A reaction tube 10 cm. long and 2·5 cm. in diameter was fitted with a side tube 7 cm. from the centre of the reaction tube itself. 100 mm. of a 1:1 $H_2 : N_2O$ mixture were passed into the tube and the reaction allowed to go for several minutes at 660° C. The water was then condensed out by cooling the side tube and the pressure of the residual H_2-N_2O-N_2 mixture determined. A similar experiment was then made except that the side tube was kept cool from the start. After making due allowance for the cooling of the side tube on the pressure of the non-condensable gases, it was found that 13·5 mm. H_2O were produced in 6 min. when H_2O was allowed to accumulate while 16·5 mm. were obtained if H_2O was removed continuously. Water vapour is therefore an inhibitor at these pressures. Similar results were obtained with a 7 cm. bulb, in these experiments the gases were removed for analysis by a Töpler pump. The rate of reaction, on allowing the H_2O to accumulate, was smaller than that in which the H_2O was removed at intervals and the gas mixture readmitted to the reaction bulb.

An approximate estimate of the stationary concentration may be made in the following way. If R is the rate of reaction (millimetres per second) and T the time in seconds required for an H_2O molecule to diffuse to the absorbing agent, the pressure of H_2O (p_{H_2O}) in millimetres will be given by

$$R \,.\, T = p_{H_2O}.$$

T can be calculated from the Einstein equation $x^2 = 2D \,.\, T$ where x is the

distance the molecule diffuses through a gas of diffusion coefficient D. Take the above example, D for 100 mm. of $H_2 : N_2O$ at 1000° K. is about 12 cm.^{2}/sec. The temperature of the gas from the centre of the bulb to the H_2O absorber is not uniformly at 1000° K. and hence D may be reduced to 10 cm.^{2}/sec. Although the $CaCl_2$ boat was 5 cm. from the centre of the bulb, x will be assumed to have a value of 7 cm. as the time for diffusion is proportional to the square of the distance. On substituting T = 2·5 sec., R = 16·5 mm./360 sec., p_{H_2O} is 0·11 mm., which is insufficient to retard the reaction to any appreciable extent or to affect the manometer readings. In the experiments to be described below, the rate did not exceed 0·2 mm./sec., nor did the pressure exceed 300 mm., in which circumstances p_{H_2O} would be 1 mm. and the retardation would not exceed 2%. The manometer would therefore indicate the pressure of H_2, N_2O and N_2, in the most adverse case, to within 1 mm. or 0·3%, which is within the limits of experimental error.

To make absolutely certain that the variation in this small stationary concentration of H_2O did not influence the reaction, a bulb was set up with a somewhat longer neck so that the $CaCl_2$ boat could be situated at a distance from the mouth of the furnace. A run was then made with the boat at the

Table I.

Temperature 655° C. 2·5 cm. diameter reaction tube.

Time.	Position I.			Position I.			Position II.		
	p_{H_2}.	$p_{total.}$	Δp.	p_{H_2}.	$p_{total.}$	Δp.	p_{H_2}.	$p_{total.}$	Δp.
min.	mm.	mm.							
0	51·0	102·0	0	52·5	103·5	0	52·0	105·0	0
1	—	100·5	1·5	—	102·0	1·5	—	103·5	1·5
2	—	97·0	5·0	—	98·5	5·0	—	100·5	4·5
3	—	93·5	8·5	—	95·5	8·0	—	96·5	7·5
4	—	90·5	11·5	—	92·5	11·0	—	93·0	12·0
6	—	88·5	16·5	—	87·5	16·0	—	88·5	16·5
8	—	81·5	20·5	—	84·5	19·0	—	84·5	20·5
10	—	79·0	23·0	—	81·5	22·0	—	81·0	24·0

furnace (position I) and a second run with the boat placed 5 cm. from its previous position (position II). In the second position the molecules would therefore require to diffuse a further 5 cm. through a *cold* gas mixture; the time of diffusion would increase about 10 times and with it the value of p_{H_2O}. As can be seen from an examination of Δp (pressure decrease) in Table I, no diminution occurs in the rate with the boat in the second position. The

reaction exhibits an induction period which is characteristic if the hydrogen is admitted to the reaction tube before the nitrous oxide.* Experiments were also made to see if any difference in results was obtained by using P_2O_5 or $CaCl_2$ as H_2O absorbent, but no variation in rate could be detected.

The method is therefore suitable for a study of the reaction provided, (*a*) the total pressure of the mixture does not exceed half an atmosphere, (*b*) the rate does not exceed 0·2 mm./sec., (*c*) the absorbing agent is close to the reaction bulb.

Results.

Comparison of Rate of Reaction with the Decomposition Rate of N_2O.—In view of the observation of Hinshelwood† that the rate of H_2O formation was no faster than the rate of decomposition of N_2O, it was of importance to determine if this occurred in the present experiment. In Table II the first experiment is a run with a 1 : 1 H_2–N_2O mixture and the second a decomposition run for N_2O at a somewhat higher pressure.

Table II.

Temperature 645° C. 5 cm. tube.

H_2–N_2O.			N_2O alone.		
t.	*p.*	Δp.	*t.*	*p.*	Δp.
0	97·0	—	0	295·4	—
0·5	93·2	3·8	5	298·0	2·4
1·0	88·8	8·2	10	300·2	4·8
1·5	84·8	12·2	15	302·4	7·0
2	81·6	15·4	20	305·0	9·6
3	77·0	20·0	25	307·4	12·0
4	73·4	23·6	30	309·0	13·6
5	71·2	25·8	35	311·4	16·0
6	68·8	28·2			
7	66·2	30·8			

On reducing the rate of decomposition of N_2O to 48·5 mm., assuming a bimolecular reaction in this pressure range, the initial rate of decomposition would be 0·026 mm./min. compared with 8·5 mm./min. of the H_2–N_2O reaction; the latter is 325 times faster than the former. In a long spiral of silica tubing, 0·4 cm. in bore, at 630°, the rate of the H_2–N_2O reaction was

* This is caused by the long neck, since the nitrous oxide requires a short time to diffuse into the reaction zone.

† 'Proc. Roy. Soc.,' A, vol. 106, p. 292 (1924).

1·5 mm./min., while that for N_2O was 0·017, the ratio being 90. Using a 7 cm. bulb at the same temperature, the respective values were 22·0 and 0·044 mm./min. or 500 : 1. (The smaller rate of N_2O decomposition in the spiral was due to part of its being close to the mouth of the furnace and therefore at a somewhat lower temperature, and to the volume of the tubing leading to the Töpler pump being comparable with that of the spiral itself.) It will be observed that the rate of the H_2–N_2O reaction relative to that of N_2O is rather greater in wider vessels. As the N_2O reaction is homogeneous at these pressures, the increase must be due wholly to the H_2–N_2O reaction.

Packing Experiments.—The effect of packing a reaction tube with the same material of which it is made provides a great deal of information about the nature of a gas reaction. If packing increases the rate, the reaction is predominantly heterogeneous; if there is no change in velocity, the reaction is probably homogeneous. On the other hand, if packing retards the rate, it may be assumed that the process involves some kind of chain mechanism, since inhibition by surfaces has been shown to be a definite characteristic of chain reactions.

A restriction is placed upon the method of carrying out the packing, for the diffusion of H_2O out of the tube must not be impeded. Silica tubes 5 cm. long and 1 cm. and 0·7 cm. external and internal diameter were employed, their

Table III.

Temperature 660°. 1 : 1 mixture.

t.	225.		226.		230.		231.	
	p.	*Δp.*	*p.*	*Δp.*	*p.*	*Δp.*	*p.*	*Δp.*
0	101·0	—	103·2	—	102·0	—	100·5	—
0·5	97·0	4·0	—	—	—	—	97·0	3·5
1	93·0	8·0	100·5	2·8	99·0	3·0	93·0	7·5
2	87·0	14·0	96·2	7·0	94·5	7·5	86·0	14·5
3	82·5	18·5	92·5	10·7	90·5	11·5	80·0	20·5
4	77·5	23·5	90·2	13·0	87·0	15·0	75·5	25·0
5	—	—	—	—	—	—	72·0	28·5
6	72·5	28·5	85·8	17·5	83·0	19·0	—	—
8	69·0	32·0	82·0	21·2	78·5	23·5	—	—

axes being set parallel to that of the reaction tube itself. On packing a 5 cm. diameter tube, 10 cm. long, half-full with 20 of these tubes and so increasing the silica surface about 3·5 times, the results in Table III were obtained. In experiment 225, the tube was empty, in 226 and 230 packed, and 231 empty

again. Additional experiments (Table IV) were also made with a 2·5 cm. tube packed completely with similar tubes thus increasing the surface about twice. In both tubes, there is a most marked inhibiting effect on packing the tube. In experiment 246 the rate is reduced to 0·4 of its value in 243 and 247. The method of packing in this case really amounted to reducing the diameter to 0·7 cm. Consequently, if it is assumed, according to the chain theory, that the rate is proportional to the square of the diameter the rate should decrease 13-fold. The reason for this wide discrepancy will be discussed below.

Table IV.

t.	243. Empty.		246. Packed.		247. Empty.	
	p.	Δp.	p.	Δp.	p.	Δp.
0	102·5	—	103·0	—	102·0	—
1	95·0	7·5	100·0	3·0	94·0	8·0
2	88·0	15·5	98·0	5·0	88·0	14·0
3	83·0	19·5	95·5	8·5	83·0	19·0
4	80·0	22·5	93·0	10·0	78·5	23·5
6	72·5	30·0	87·0	16·0	72·0	30·0
8	69·5	33·0	84·5	18·5	68·0	34·0
10	67·0	35·0	82·5	20·5	66·0	36·0

The results could be reproduced within about 10% over a period of several weeks; in individual series, better agreement could be obtained. It may be added, however, that on first putting into use a tube which had not been employed for some time, the reaction velocity for the first run was consistently smaller (in some experiments as much as 50%) than that of the next run, after which it remained sensibly constant, although the tube was baked out in a vacuum of 10^{-5} mm.

Effect of Total Pressure.—A 1 : 1 mixture was employed for these experiments and the total pressure did not exceed 300 mm. as is required by the calculations made above. The initial rate (R) of reaction is nearly proportional to the pressure (p) as is shown in Table V by the constancy of the value of R/p. Unimolecular constants (k) were therefore calculated for each run; the figures obtained are reasonably constant, at least during the first half of the reaction. When making these calculations, a slight correction was applied, since, if the $\Delta p - t$ (Δp = pressure decrease, t = time) curves are plotted the reaction exhibits a slight induction period of about 5 sec. The times used to calculate k were therefore reduced by 0·1 min. Similarly R was

Table V.

Temperature 628°. 5 cm. tube.

138.				139.			
t.	*p.*	Δp.	k (sec.$^{-1}$ $\times 10^3$).	*t.*	*p.*	Δp.	k.
0	254·0	—	—	0	200·0	—	—
0·5	251·0	3·0	—	0·5	197·6	2·4	—
1·0	247·0	7·0	1·04	1·0	194·2	5·8	1·11
1·5	242·8	11·2	1·30	2·0	187·2	12·8	1·22
2	238·0	16·0	1·19	3	181·0	19·0	1·22
3	229·6	24·4	1·24	4	174·4	25·6	1·27
4	221·4	32·6	1·28	5	168·6	31·4	1·30
5	214·2	39·8	1·29	6	163·4	36·6	1·25
6	207·2	46·8	1·31	8	155·0	45·0	1·27
8	196·4	57·6	1·28	10	148·4	51·0	1·23
R 8·5 mm./min.				6·6			
R/p 0·034				0·033			

140.				134.			
t.	*p.*	Δp.	k.	*t.*	*p.*	Δp.	k.
0	148·0	—	—	0	99·4	—	—
0·5	146·2	1·8	—	1	96·0	3·4	—
1·0	143·2	4·8	1·28	2	92·4	7·0	1·30
1·5	140·4	7·4	1·27	3	89·4	10·0	1·38
2	137·8	10·2	1·22	4	86·8	12·6	1·25
3	132·6	15·4	1·32	5	84·4	15·0	1·23
4	128·0	20·0	1·30	6	83·0	16·4	1·14
5	124·0	24·0	1·34	8	79·8	19·6	1·07
6	120·8	27·2	1·30	10	77·4	22·0	0·95
8	115·0	33·0	1·30	12	76·0	23·4	0·90
10	112·0	36·0	1·13				
R 5·4				3·4			
R/p 0·037				0·034			

163.

t.	*p.*	Δp.	k.
0	51·0	—	—
1	49·0	2·0	1·33
2	46·8	4·2	1·49
3	45·0	6·0	1·49
4	43·0	8·0	1·57
5	41·8	9·2	1·50
6	41·0	10·0	1·39
8	39·6	11·4	1·24
10	30·2	12·8	1·17
R 2·2			
R/p 0·043			

obtained by measuring the slope of the tangent to the $\Delta p - t$ curve extrapolated back to $\Delta p = 0$.

Effect of Nitrous Oxide and of Hydrogen.—In order to determine the effect of the gases separately, the following experiments were made: (*a*) p_{H_2} varying from 25–200 mm., for $p_{N_2O} = 50$ and for $p_{N_2O} = 200$ (Tables VI and VII); (*b*) p_{N_2O} varying from 25–150 mm. for $p_{H_2} = 50$ and for 150 mm., Table VIII and fig. 4. respectively. Fig. 2 shows how the initial rate varies with hydrogen

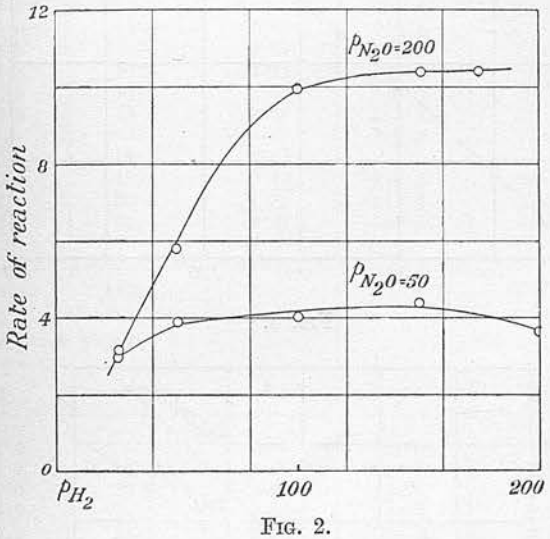


FIG. 2.

pressure. When p_{N_2O} is 50 mm., there is only a small increase from $p_{H_2} = 25$ to 50, and thereafter R is very nearly constant. On the other hand, if $p_{N_2O} =$ 200, the rate increases quite rapidly to a maximum which is reached at a higher value of p_{H_2}, viz., 100 mm.

In fig. 3 it is observed that R is almost proportional to p_{N_2O} except that at higher pressures there is a tendency for the R — p_{N_2O} curve to bend over. That the results for the 1 : 1 mixture conform closely to a unimolecular equation is thus mainly due to the nitrous oxide. In Tables VI and VII, the value of k has been calculated on the assumption that the kinetics of the reaction are given accurately by the equation $-dp_{N_2O}/dt = kp_{N_2O}$. In accordance with the effect of H_2 when p_{N_2O} is 200 mm. (fig. 3), it will be seen that in Table IV the value of k decreases rapidly in runs 142 and 143, whereas in 144–146 the decrease is less marked. Further, the initial value of k increases until p_{H_2} reaches 100 mm. and then remains constant. When p_{N_2O} is small as in Table VII, the effect of p_{H_2} is also small and k remains fairly constant in an individual run and throughout the series.

Effect of Nitrogen and of Argon.—Since the value of k in Table V does not change during the course of the reaction, nitrogen must have practically no influence on the rate. Separate experiments were, however, made with nitrogen

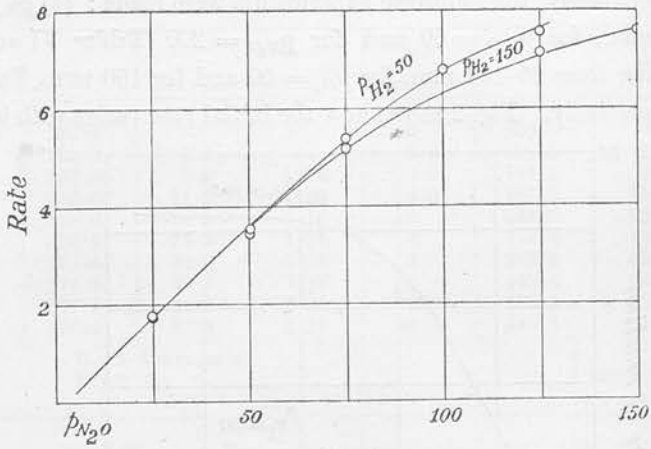


FIG. 3.

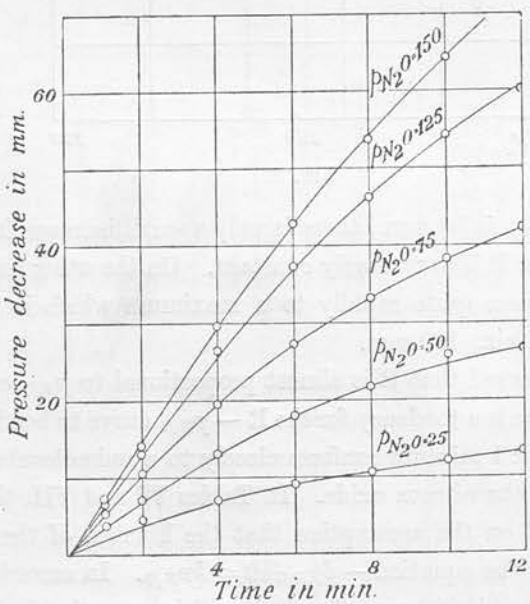


FIG. 4.

and with argon in order to confirm this supposition. As the results in Table IX demonstrate, no measurable effect could be detected. The absence of inhibition incidently provides evidence for the validity of the method of observation, for although the inert gas impedes the diffusion of H_2O from the

Table VI.

Effect of p_{H_2} (p_{N_2O} = 200 mm.) 615°. 5 cm. tube.

142.				143.		
p_{H_2} 25·0, p_{N_2O} 199·4.				p_{H_2} 50·0, p_{N_2O} 201·8.		
t.	*p.*	Δp.	*k.*	*p.*	Δp.	*k.*
0	224·6	—	—	251·8	—	—
1	221·6	3·0	2·81	246·4	5·4	5·28
2	218·0	6·6	2·91	240·0	11·8	5·75
3	224·0	10·6	3·11	233·0	18·8	5·86
4	212·0	12·6	2·77	228·0	23·8	5·53
5	209·8	14·8	2·66	223·4	28·4	5·32
6	—	—	—	220·2	31·6	4·93
7	206·4	18·2	2·33	—	—	—
8	205·2	19·4	2·14	215·2	36·6	4·36
10	204·0	20·6	1·82	212·2	39·6	3·75
12	203·2	21·4	1·61	210·4	41·6	3·20

144.				145.		
p_{H_2} 99·4, p_{N_2O} 202·2.				p_{H_2} 150·8, p_{N_2O} 202·2.		
t.	*p.*	Δp.	*k.*	*p.*	Δp.	*k.*
0	301·6	—	—	351·0	—	—
1·0	294·2	7·4	8·88	344·2	6·9	—
1·5	289·0	12·6	8·92	339·0	12·0	8·43
2·0	283·2	18·4	9·08	334·2	16·8	8·52
2·5	277·4	24·2	9·73	328·8	22·2	8·78
3·0	271·6	30·0	9·42	323·8	27·2	8·88
4·0	261·0	40·6	10·20	314·0	37·0	9·08
5·0	253·0	48·6	9·75	304·8	46·2	9·18
6·0	245·0	56·6	9·67	297·0	54·0	9·07
7·0	239·2	62·4	9·16	289·0	62·0	9·10
8·0	234·0	67·6	8·31	281·2	69·8	9·14
10·0	227·2	74·4	7·88	269·2	81·8	8·95

146.

p_{H_2} 178·4, p_{N_2O} 200·8.

t.	*p.*	*p.*	*k.*
0	379·2	—	—
1·0	371·8	7·4	—
1·5	367·2	12·0	8·54
2·0	361·2	18·0	9·25
2·5	356·6	22·6	9·07
3	350·0	29·2	9·68
4	341·0	38·2	9·51
5	331·4	47·8	9·62
6	322·8	56·4	9·63
7	314·0	65·2	9·77
8	307·0	72·2	9·67
10	288·6	85·6	9·69

Table VII.

129.				130.			131.		
p_{N_2O} 50·0, p_{H_2} 202·0.				p_{N_2O} 50·6, p_{H_2} 150·0.			p_{N_2O} 50·0, p_{H_2} 100·2.		
t.	*p.*	Δp.	*k.*	*p.*	Δp.	*k.*	*p.*	Δp.	*k.*
0	252·0	—	—	200·8	—	—	150·2	—	—
1	248·4	3·6	1·37	196·6	4·2	1·62	144·6	5·6	1·95
2	244·8	7·2	1·35	192·4	8·4	1·58	141·2	9·0	1·74
3	241·8	10·8	1·40	189·0	11·8	1·53	138·0	12·2	1·69
4	238·0	14·0	1·40	186·0	14·8	1·47	135·0	15·2	1·58
6	231·8	20·2	1·45	181·4	19·4	1·36	130·4	19·8	1·42
8	227·8	24·2	1·39	178·0	22·8	1·36	127·0	23·2	1·31
10	223·8	28·2	1·36	175·2	25·6	1·17	124·4	25·8	1·21
12	—	—	—	173·2	27·8	1·10	122·8	27·4	1·11

132.				133.		
p_{N_2O} 50·6, p_{H_2} 50·4.				p_{N_2O} 50·0, p_{H_2} 25·0.		
t.	*p.*	Δp.	*k.*	*p.*	Δp.	*k.*
0	101·0	—	—	75·0	—	—
1	97·2	3·8	1·34	72·4	2·6	0·98
2	93·2	7·8	1·45	69·0	6·0	1·11
3	90·4	10·6	1·33	66·6	8·4	1·06
4	87·6	13·4	1·31	64·0	11·0	1·06
6	83·8	17·2	1·17	60·0	15·0	1·01
8	80·6	20·4	1·19	58·0	17·0	0·88
10	78·4	22·6	1·00	55·4	19·6	0·84
12	76·4	24·6	0·93	54·0	21·0	0·76

Table VIII.

Effect of p_{N_2O} (p_{H_2} = 50 mm.). 615°.

147.			148.		153.	
p_{H_2} 50·0, p_{N_2O} 25·2.			p_{H_2} 50·2, p_{N_2O} 49·8.		p_{H_2} 50·4, p_{N_2O} 75·2.	
t.	*p.*	Δp.	*p.*	Δp.	*p.*	Δp.
0	75·2	—	100·0	—	125·2	—
1	74·2	1·0	97·0	3·0	121·4	3·8
2	72·4	2·8	93·6	6·4	115·8	9·4
3	71·2	4·0	90·0	10·0	110·2	15·0
4	69·4	5·8	86·2	13·8	106·0	19·2
5	68·0	7·2	84·0	16·0	101·8	23·4
6	66·8	8·4	81·4	18·6	97·6	27·6
8	65·0	10·2	78·0	22·0	91·2	34·0
10	63·2	12·0	75·0	25·0	87·0	38·2
12	62·0	13·2	73·2	26·8	83·4	41·8

Table VIII—(continued).

149.			152.	
	p_{H_2} 50·4, p_{N_2O} 100·6.		p_{H_2} 50·2, p_{N_2O} 124·8.	
t.	*p.*	Δp.	*p.*	Δp.
0	151·0	—	174·8	—
1	146·0	5·0	169·0	5·8
2	139·2	11·8	161·4	13·4
3	131·2	19·8	154·2	20·6
4	126·4	24·6	147·8	27·0
5	120·8	30·2	142·6	32·2
6	116·2	34·8	139·0	35·8
8	110·0	41·0	134·8	40·0
10	107·0	44·0	132·2	42·6
12	105·4	45·6		

Table IX.

Effect of N_2. 615°. 1 : 1 Mixture.

$p$mix.	100·2	99·8	99·6	100·2
p_{N_2}.	0	90·0	50·2	25·8
t.	Δp.	Δp.	Δp.	Δp.
1	3·2	3·0	3·2	3·4
2	8·0	6·8	7·4	7·4
3	11·4	9·8	11·8	11·2
4	15·0	13·0	14·2	14·2
5	17·2	15·6	16·8	17·2
6	19·4	17·8	19·0	19·6
8	23·0	20·8	22·8	23·0
10	25·4	23·6	25·6	25·8
12	27·4	25·8	—	27·8

Effect of Argon. 615°. 1 : 1 Mixture.

$p$mix.	99·4	98·8	101·6	100·4
p_A.	—	152·2	80·4	40·0
t.	Δp.	Δp.	Δp.	Δp.
1	3·4	2·8	3·0	3·4
2	7·0	6·0	7·2	7·0
3	10·0	9·0	12·2	10·2
4	12·6	11·6	14·8	13·0
5	15·0	14·6	16·2	15·4
6	16·4	16·2	18·8	17·4
8	19·6	19·4	22·0	20·4
10	22·0	22·0	25·0	23·0
12	23·4	24·0	27·0	—

reaction zone to the P_2O_5 and so increases the stationary concentration of H_2O, the increase is not sufficient to retard the reaction appreciably. This is to be expected from the rough calculations made previously.

Temperature Coefficient.—It has been shown in Table II that the rate of the H_2–N_2O reaction at 645° is considerably faster than the rate of decomposition of the nitrous oxide. The relative rates of the two reactions would only remain the same at different temperatures if their temperature coefficients are identical. It was consequently of importance to determine the temperature coefficient of the H_2–N_2O reaction. The apparent energy of activation (E) was calculated from the approximate equation $d\,ln\,R/dT = E/RT^2$. The value of E, viz., 32·5 k.cal., is much smaller than that for the decomposition of N_2O which is 54 k.cal. As the temperature is raised, therefore, the relative rates of the H_2–N_2O and the N_2O reaction will decrease and at some high temperature may eventually become equal.

Explosions.—Inflammation of the mixture could readily be obtained if the pressure or the temperature were sufficiently raised. For example, taking the results in Table X, at 700°, on increasing the pressure beyond 200 mm., the mixture exploded provided the gases were admitted quickly; on slow admission, no explosion could be obtained probably because of the rapid

Table X.

Temperature coefficient 1 : 1 Mixture. Total pressure 200 mm.

Experiment.	Temp.	R.
	° C.	
110	700	25
111	638	13
112	597	5·1
113	540	1·0

E 32·5 k.cal.

disappearance of H_2 and of N_2O. Similarly, explosions could be observed in the following way. The reaction tube was attached to another bulb (volume two or three times that of the tube) which could be filled with mercury thus increasing the pressure in the tube. If, during the course of a run (*e.g.*, similar to experiment 110) the mercury was suddenly admitted to the bulb, explosion occurred. On the other hand, if compression were gradual no such explosion took place. Indeed, it appeared that the condition for explosion depended on the reaction rate exceeding a certain value. The limit it thus quite different from that in the H_2–O_2 reaction where the transition from an

extremely slow reaction to explosion is comparatively abrupt. Attempts were also made to discover the existence of an upper limiting pressure for explosion, adopting the methods employed in the H_2–O_2 reaction, but no indication of this phenomenon could be observed.

Discussion of Results and Mechanism of the Reaction.

The first decision to be made from these experiments concerns the class to which the mechanism of the reaction belongs. That the reaction consists of the decomposition of N_2O followed by oxidation of H_2 (No. 3, p. 526) must be excluded since the observed rate of production of water is much faster than the decomposition rate of N_2O. The inhibitory influence of surfaces rules out the possibility of the bimolecular reaction. Further, a bimolecular reaction having an energy of activation of 30 k.cal. would be measurable at a temperature of 300°–400° instead of about 600°. The inhibition by surfaces likewise eliminates the purely heterogeneous reaction. There remains, then, the chain mechanism, but although the present reaction is placed in this class by a process of elimination, there is definitely positive evidence of chain characteristics. In a chain reaction, the first three types may be incorporated for (*a*) initiation may be the result of a heterogeneous* or of a homogeneous reaction† as is the case in the H_2–O_2 reaction, (*b*) termination may take place in the gas or at a surface, (*c*) propagation most likely involves a series of bimolecular encounters but the possibility of ternary collisions may also require to be taken into account.

The best evidence for the chain hypothesis is the increase in rate in wider vessels. The explosive nature of the reaction also points to the chain hypothesis being the correct one to employ. Before any quantitative scheme can be constructed, the nature of the carriers must be known. While direct evidence is, in most cases, extremely difficult to obtain, there are usually only a small number of possibilities when dealing with a comparatively simple reaction such as the one under discussion.

One of the simplest schemes is as follows :—

$$H + N_2O \rightarrow OH + N_2 + 75{\cdot}5 \text{ k.cal.}$$
$$OH + H_2 \rightarrow H_2O + H,$$

* Alyea and Haber, 'Z. phys. Chem.,' B, vol. 10, p. 193 (1931); Alyea, 'J. Amer. Chem. Soc.,' vol. 53, p. 1324 (1931); Melville and Ludlam, 'Proc. Roy. Soc.,' A, vol. 135, p. 315 (1932).

† Haber and Oppenheimer, 'Z. phys. Chem.,' B, vol. 16, p. 443 (1932); Taylor and Salley, 'J. Amer. Chem. Soc.,' vol. 55, p. 96 (1933).

the carriers being H and OH as in the H_2–O_2 reaction, H or OH being generated by some primary reaction. It is known that hydrogen atoms attack nitrous oxide* with the eventual production of water; there is thus evidence for the first step. Proof of the second is not so direct, but there is a considerable body of opinion in favour of OH reacting with H_2,† especially at high temperatures, as papers on the H_2–O_2 reaction demonstrate. OH radicals occur in the flame of H_2 burning in N_2O‡ but this, of course, is not a proof but only an indication that they may occur in the stable reaction. If a stationary concentration of OH be set up, it should be possible by the use of a dynamic method to sweep these radicals out of the reaction tube and so obtain hydrogen peroxide in a cooled trap.§

There is now the question of initiation to be considered. In the corresponding H_2–O_2 reaction, homogeneous initiation seems to require so much activation at temperatures below 560°, it appears that a surface reaction is responsible for the provision of reaction centres.|| With H_2–N_2O mixtures, there is a source of O atoms in the gas on account of the unimolecular decomposition of N_2O, and, as O atoms react with H_2 readily at 600°,¶ initiation may occur as follows:—

$$N_2O + N_2O \rightarrow N_2O' + N_2O \qquad k_1$$

$$N_2O' \rightarrow N_2 + O$$

or

$$H_2 + N_2O \rightarrow N_2O' + H_2 \qquad k_2$$

$$N_2O' \rightarrow N_2 + O$$

followed by

$$O + H_2 \rightarrow OH + H \qquad k_3$$

k_1, k_2 and k_3 being velocity coefficients. Activation by hydrogen is included since H_2 may behave similarly to other inert gases in this respect. If the collisions of H_2 with N_2O are particularly efficient in activating N_2O, as is the

* Taylor, 'Trans. Faraday Soc.,' vol. 21, p. 560 (1926).

† *Cf.* in particular, Bonhoeffer and Haber, 'Z. phys. Chem.,' vol. 137, p. 337 (1928); Frankenburger and Klinkhardt, *ibid.*, B, vol. 15, p. 421 (1932).

‡ Fowler and Badami, 'Proc. Roy. Soc.,' A, vol. 133, p. 325 (1931).

§ Pease, 'J. Amer. Chem. Soc.,' vol. 52, p. 5106 (1930); vol. 53, p. 3188 (1931); Bates and Salley, *ibid.*, vol. 55, p. 110 (1933).

|| Alyea, *loc. cit.*; also Goldman, 'Z. phys. Chem.,' B, vol. 5, p. 316 (1929).

¶ Harteck and Kopsch, 'Z. Electrochem.,' vol. 36, p. 714 (1930); 'Z. phys. Chem.,' B, vol. 12, p. 327 (1931).

case with many other unimolecular reactions,* it may be that initiation is wholly dependent on this encounter.

The termination of the chains may occur by $H + H \rightarrow H_2$, $OH + OH \rightarrow H_2O_2$, or $H + OH \rightarrow H_2O$, these processes requiring the presence of a third molecule or a surface. That surface combination does not wholly control termination is shown by the comparatively small influence of packing. Consequently, most of the termination occurs in the gas. Setting up the equations for the stationary concentrations of H and of OH, then,

$$\frac{d[H]}{dt} = I + k_5[OH][H_2] - k_4[H][N_2O] - k_6[H]^2[X] - k_7[H][OH][X] = 0,$$

$$\frac{d[OH]}{dt} = I + k_4[H][N_2O] - k_5[OH][H_2] - k_8[OH]^2[X] - k_7[H][OH][X] = 0,$$

where I is the rate of initiation, X is a third molecule. Surface combination has been neglected for a first approximation. Solution of these equations would be extremely difficult since they are both quadratic. A great simplification can be made if it be assumed that $k_5 \gg k_4$, in which case the stationary concentration of H atoms would greatly exceed that of OH, $k_7[H][OH][X]$ could then be neglected. Further, according to Bonhoeffer and Pearson† instead of

$$\begin{aligned} OH + OH + X &\rightarrow H_2O_2 + X, \\ OH + OH &\rightarrow H_2O + O \end{aligned}$$

which would be followed by

$$\begin{aligned} O + H_2 &\rightarrow OH + H \\ OH + H_2 &\rightarrow H_2O + H \end{aligned}$$

and the chain would not be terminated by the disappearance of two OH radicals in this way. $k_8[OH]^2[X]$ could also be neglected. Therefore

$$[H] = (2I/k_6[X])^{\frac{1}{2}} \text{ and } [OH] = I/k_5[H_2] + \frac{k_4[N_2O]}{k_5[H_2]}\left(\frac{2I}{k_6[X]}\right)^{\frac{1}{2}},$$

$$-\frac{d[N_2O]}{dt} = k_4[N_2O](2I/k_6[X])^{\frac{1}{2}},$$

if the chains are long. $I = [N_2O]\{k_1[N_2O] + k_2[H]\}$. Since nitrogen and argon have no effect, it will be supposed that compared with N_2O and H_2 they are inefficient in promoting the stability of the newly formed H_2 molecule.

* *Cf.* Rice, 'Chem. Rev.,' vol. 10, p. 127 (1932).

† 'Z. phys. Chem.,' B, vol. 14, p. 1 (1931).

This absence of inhibition may in part be due to the inert gas impeding the diffusion of H atoms to the walls and so tending to increase the rate. To a first approximation, it will be assumed that $[X] = [N_2O] + [H_2]$, so that the equation expressing the kinetics of the reaction becomes

$$-\frac{d[N_2O]}{dt} = k_4[N_2O]\left(\frac{2[N_2O]\{k_1[N_2O] + k_2[H_2]\}}{k_6\{[N_2O] + [H_2]\}}\right)^{\frac{1}{2}}.$$

An inhibiting influence of N_2O might also occur in virtue of the reaction $H + H + N_2O \rightarrow H_2O + N_2 + 180$ k.cal. for, owing to the production of two molecules after the reaction, the 180 k.cal. might be equally divided between the two and would therefore be insufficient to dissociate the H_2O molecule into H and OH. This latter process requires some 103 k.cal.

Some information about the relative magnitudes of k_1 and k_2 may be obtained from the effect of hydrogen on the rate. $k_1 \neq k_2$ as H_2 would then have no effect. In order to account for the rate reaching a maximum which maximum is attained at a lower pressure of H_2 when N_2O is small, k_1 must be considerably less than k_2. From the results of Volmer and Bogdan* on the variation of the efficiency of activation collisions with mass in the monatomic gas series, it might be expected that the collisions between H_2 and N_2O would be about as effective as those between N_2O molecules themselves. k_2 would then be $2{\cdot}5$ times that of k_1 on account of the greater collision frequency of the partners H_2 and N_2O.

The same result could be obtained if it be assumed that $k_1 = k_2$ and that N_2O is much more efficient in participating in ternary collisions than is H_2. There is, however, no reason to suppose that this is the case ; in fact, on making the calculations for the number of ternary collisions of $H + H + N_2O$ and of $H + H + H_2$, it was found that the latter was about 20% greater than the former.

When $[H_2]$ is so great that the rate becomes independent of it, the order with respect to $[N_2O]$ is 3/2 and thus is slightly higher than the observed order of unity.

If termination had occurred mainly by the combination of two OH radicals in a ternary collision then the kinetic equation would have become

$$-\frac{d[N_2O]}{dt} = k_5[H_2]\left(\frac{2[N_2O]\{k_1[N_2O] + k_2[H_2]\}}{k_8\{[N_2O] + [H_2]\}}\right)^{\frac{1}{2}},$$

which is definitely not in agreement with observation.

* 'Z. phys. Chem.,' B, vol. 21, p. 271 (1933).

According to this interpretation, the relative rate of the H_2–N_2O reaction to that of the N_2O decomposition does not represent exactly the chain length. For a 1 : 1 mixture the ratio would require to be reduced by 3·5 in view of the rate of activation due to H_2. As each O atom is responsible for the initiation of two chains, the reduction factor would amount to 1/7.

Since the rate of the H_2–N_2O reaction increases with the first power of the pressure (for a 1 : 1 mixture) and the rate of starting of the chains with the square of the pressure, the chain length will decrease as the total pressure increases. The reaction has thus been studied virtually in a region above the upper limit of a chain explosion. Had such an explosion been possible, then on reducing the pressure inflammation should have resulted, but no indication of this phenomenon was observed.

The mechanism of the reaction, as suggested by these experiments, can be summarized in broad outline as follows. The reaction is of the chain type initiated by O atoms derived from the thermal dissociation of N_2O molecules and propagated by H atoms and OH radicals. Termination occurs mainly in the gas by combination of H atoms, but some may take place on the walls.

The author wishes to thank Dr. E. B. Ludlam for his encouragement, the Carnegie Trustees for a scholarship and the Moray Fund Committee of the University of Edinburgh for a grant for silica apparatus.

Summary.

The kinetics of the reaction between hydrogen and nitrous oxide have been investigated at pressures from 50–400 mm. and temperatures from 550°–700° C. in silica bulbs.

The rate of reaction is much faster than that of the decomposition of nitrous oxide. The products are mainly N_2 and H_2O. The rate is directly proportional to the pressure of nitrous oxide and nearly independent of that of H_2 except when the pressure of N_2O is high. The reaction goes faster in wider vessels, but the increase is not proportional to the square of the diameter. The apparent energy of activation is 32 k.cal. Nitrogen and argon have no effect.

The chain mechanism suggested to explain these results is :—

(*a*) Initiation—

$$N_2O + N_2O \rightarrow N_2O' + N_2O,$$
$$N_2O + H_2 \rightarrow N_2O' + H_2,$$
$$N_2O' \rightarrow N_2 + O,$$
$$O + H_2 \rightarrow OH + H.$$

(*b*) Propagation—

$$H + N_2O \rightarrow OH + N_2,$$
$$OH + H_2 \rightarrow H_2O + H.$$

(*c*) Termination—

$$H + H + X \rightarrow H_2 + X,$$

X being a third molecule or a wall.

Explosions may also occur if the pressure and temperature are high enough, but no sharp explosion limits could be obtained, such are characteristic of chain reactions.

HARRISON AND SONS, Ltd., Printers, St. Martin's Lane, London, W.C.2.

Reprinted from the Journal of the Chemical Society, 1934.

66. *The Oxidation of Phosphine in Presence of Tungsten and Molybdenum.*

By H. W. Melville and H. L. Roxburgh.

In a previous paper (J., 1933, 586) we described the investigation of the kinetics of the thermal decomposition of phosphine on tungsten and molybdenum as a preliminary to the study of the oxidation at pressures below the lower critical explosion limit. The purpose of the present experiments was to determine if the oxidation was a chain reaction, the chains being started on the filament and terminated on the walls of the reaction vessel, as with phosphorus–oxygen mixtures (Melville and Ludlam, *Proc. Roy. Soc.*, 1932, *A*, **135**, 516). Further, it was suggested, to account for the formation of red phosphorus in the decomposition, that P_2 molecules may evaporate off the filament. As it has been shown that such molecules initiate chains in phosphorus–oxygen mixtures, it was expected that they might also provide reaction centres for the chain oxidation of phosphine. On the other hand, as oxygen is strongly adsorbed on a tungsten surface, it is possible that the decomposition of phosphine would be markedly inhibited, and that the phosphorus formed would undergo a purely surface oxidation without giving rise to chain-initiating molecules. Other possibilities are discussed below (p. 270).

Three criteria exist whereby the chain character of the reaction may be determined, (*a*) the appearance of a glow, the intensity of which is proportional to the rate of oxidation, (*b*) the acceleration of the reaction by use of wider tubes, and (*c*) the acceleration produced by the addition of inert gases. These criteria are fulfilled in the oxidation of phosphorus. Suppose, however, that an appreciable part of the reaction took place on the surface of the filament, exclusive of the small proportion of the heterogeneous reaction required to start the chains; the glow would still be observed, but the rate of the reaction would no longer be proportional to the square of the reaction-vessel diameter, nor would the acceleration by inert gases be so marked. Owing to the variation in the condition of the surface of the reaction tube, it is sometimes difficult to verify the diameter law, and therefore in the present instance, the inert-gas effect has been used to determine what fraction, if any, consisted of a chain process. This acceleration by inert gases can be calculated from experiments on the effect of the gas on the lower explosion limit, for it has been shown in the phosphorus experiments (*loc. cit.*, p. 327) that the observed increase in velocity is in agreement with the value calculated from the diffusion theory.

Experimental.

The apparatus was identical with that described in the first paper, and the same type of divided filament was used to measure its temperature. The pressures which could be employed were, of course, now restricted by the occurrence of explosion at 1 mm. for the 1 : 1 mixture. An oil manometer was used for the majority of the experiments. Both molybdenum and tungsten were apparently unattacked by the products of the reaction for, on examination of the filament surface by a microscope, no pitting or roughening could be observed, and the diameter remained the same throughout a long series of experiments. It was observed, however, that the activity of the wire gradually diminished with use, but could easily be restored by heating in a vacuum at about 1000° for a few minutes. Between each run, the filament was glowed at this temperature, and it will be shown below that this procedure renders the results reproducible within fairly close limits.

A difficulty appears when the method of measuring the rate of reaction is considered, for the nature of the products depends on the relative proportions of the phosphine–oxygen mixture. When oxygen is in deficit, the reaction is mainly $PH_3 + O_2 \longrightarrow HPO_2 + H_2$, whereas with a large excess a more highly oxidised phosphorus acid is obtained and the amount of hydrogen produced is not proportional to that of oxygen used. With equivalent proportions, the rate might be measured by finding the decrease in phosphine or oxygen pressure, or alternatively, the increase in hydrogen pressure. In addition, as HPO_2 has an inappreciable vapour pressure as measured by the oil manometer, there will be a decrease in pressure during the reaction which may also be used as a measure of its extent. To find which of these methods would prove most suitable, analyses were made of the phosphine–hydrogen–oxygen mixtures at various stages in

the reaction and with different proportions of phosphine and of oxygen. The phosphine was removed with liquid air, and the hydrogen–oxygen mixture withdrawn by the Töpler pump through a small tube fitted with a platinum filament and containing calcium chloride. The filament was heated until there was no further pressure change. Oxygen was then added and another combustion made in order to determine whether the residual gas after the first combustion was hydrogen or oxygen.

TABLE I.

Temp. of filament, 836° K.; * length, 15 cm.; diam., 0·01 cm.; vol. of apparatus 230 c.c.; press. in mm. Hg.

Expt. No.	t.	p_{PH_3}.	p_{O_2}.	Final press.	Δp.	$p_{N.C.}$.†	Δp_{PH_3}.	p_{H_2}.	p_{H_2}
176	1	0·405	0·200	0·567	0·038	0·200	0·037	0·089	0·1
177	2	0·400	0·199	0·544	0·055	0·212	0·068	0·136	0·1
180	4	0·409	0·188	0·531	0·066	0·231	0·109	0·159	0·1
179	8	0·409	0·197	0·517	0·089	0·286	0·178	0·220	0·1
181	1	0·412	0·098	0·497	0·013	0·105	0·020	0·062	0·0
182	2	0·416	0·097	0·494	0·019	0·133	0·055	0·089	0·0
183	4	0·400	0·097	0·476	0·021	0·160	0·084	0·119	0·0
184	8	0·409	0·097	0·486	0·020	0·221	0·144	—	–
186	1	0·413	0·784	0·874	0·322	0·660	0·198	0·196	0·1
187	2	0·416	0·778	0·756	0·443	0·611	0·276	0·181	0·1
188	4	0·411	0·768	0·628	0·551	0·557	0·340	0·215	0·1
189	8	0·411	0·753	0·582	0·582	0·546	0·375	0·230	0·1

The measured reaction velocity is due to both filaments.

* Temperature of the central portion of the long filament.

† $p_{N.C.}$ = Press. of non-condensable gas.

Table I gives the complete results for a number of runs with a molybdenum filament, time (t) being expressed in minutes. The procedure was as follows: Phosphine was passed into the reaction tube and its pressure measured; this was followed by oxygen; the filament was heated for the required time, and the pressure again determined. Liquid air was applied to a small side tube to condense the phosphine in order to find the pressure of hydrogen and oxygen. As the vapour pressure of phosphine at liquid-air temperatures is only 0·007 mm., the pressures read on the manometer were reduced by this amount. Suitable small corrections were also applied to the observed pressure of non-condensable gas owing to cooling of the side tube in which the phosphine was frozen out. Δp is the change in total pressure and Δp_{PH_3} the decrease in phosphine pressure calculated from the manometer readings. Unfortunately, the analysis of the hydrogen–oxygen mixtures was not very accurate, for after compression into the combustion bulb, the pressure was only about 10 mm. or less; the results are probably only accurate to 10%.

Had the reaction proceeded according to the equation $PH_3 + O_2 \longrightarrow H_2 + HPO_2$, the pressure of non-condensable gas should have remained constant, whereas, as can be seen from Table I, it increases to about double its value when the oxygen pressure is one fourth that of phosphine (Expts. 181—184). In experiments 176—179, where the oxygen pressure is one half that of phosphine, $p_{N.C.}$ does not increase so quickly, and finally, when $O_2 : PH_3 = 2 : 1$, $p_{N.C.}$ actually decreases. In the first case then, there must be some decomposition of the phosphine accompanying the oxidation, and in the last, part of the hydrogen will probably be oxidised to water. These conclusions are supported by the hydrogen–oxygen analyses, for in Nos. 181–184 the value of p_{H_2} increases during the course of the reaction, but in Nos. 186—189, *i.e.*, with p_{O_2} high, although p_{O_2} steadily falls there is no corresponding increase in p_{H_2}. It is evident that the decrease in total pressure (Δp) cannot be used as a measure of the rate of reaction. This can best be seen in Expts. 181—184, where Δp remains almost constant after 2 minutes, although the change in the pressure of phosphine shows that the reaction is still proceeding.

The best measure of the rate of reaction would appear to be the change in the phosphine pressure, with the reservation that, in comparing the rates with different proportions of phosphine and oxygen, the initial rate would probably be a better approximation than determining the time required for a definite fraction of the phosphine to react.

For comparison, a similar set of experiments with a tungsten filament is given in Table II. The results are essentially similar; even with a 1 : 1 mixture, there is no very close correspondence between Δp, Δp_{PH_3}, and p_{H_2}, which would be the case if hydrogen and HPO_2 were the only products. In subsequent experiments to determine the kinetics of the reaction, analysis of the

ixture was effected by condensing out the phosphine, after which the side tube was warmed, nd a short time (5 mins.) allowed for the gases to mix completely before the current was started the filament again.

TABLE II.

Temp. of filament 768° K. Dimensions as in Table I.

Expt. No.	t.	p_{PH_3}.	p_{O_2}.	Final press.	Δp.	$p_{N.C.}$.	Δp_{PH_3}.	p_{H_2}.	p_{O_2}.
232	2	0·397	0·401	0·734	0·064	0·382	0·045	0·047	0·335
233	4	0·405	0·401	0·709	0·097	0·367	0·063	0·075	0·292
234	8	0·403	0·400	0·591	0·212	0·358	0·170	0·132	0·226
235	2	0·397	0·159	0·535	0·021	0·167	0·029	0·032	0·135
236	4	0·402	0·160	0·530	0·032	0·168	0·040	0·081	0·087
237	8	0·397	0·159	0·499	0·055	0·184	0·080	0·122	0·061
238	2	0·411	0·747	1·087	0·071	0·742	0·066	0·114	0·628
239	4	0·409	0·743	1·003	0·149	0·720	0·126	0·176	0·543
240	8	0·407	0·745	0·955	0·198	0·706	0·158	0·237	0·469

In Table I, the pressure of phosphine remained constant and that of oxygen was varied; in Table III, some additional runs are recorded as well as a decomposition run in order to find by how much the rate of oxidation was faster than the decomposition. Table IV gives a number of experiments in which the pressure of oxygen remained constant and that of phosphine was varied.

TABLE III.

Same experimental conditions, molybdenum filament.

	p_{PH_3}, 0·425; p_{O_2}, 0·406.			p_{PH_3}, 0·403; p_{O_2}, 0·095.			p_{PH_3}, 0·403.
t.	p.	p_{PH_3}.	Δp_{PH_3}.	p.	p_{PH_3}.	Δp_{PH_3}.	Δp_{PH_3}.
0	0·831	0·425	—	0·498	0·403	—	—
1	0·702	0·336	0·089	0·488	0·373	0·030	0·020
2	0·635	0·283	0·142	0·476	0·349	0·054	0·028
4	0·574	0·224	0·201	0·466	0·310	0·093	0·061
8	0·515	0·151	0·274	0·464	0·265	0·138	0·137

TABLE IV.

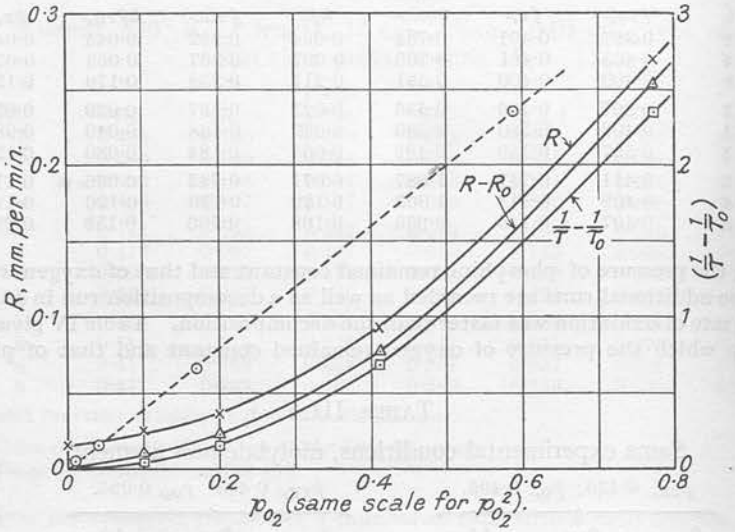
p_{PH_3}	0·114			0·200			0·782			0·397		
p_{O_2}	0·376			0·376			0·372			0·371		
t.	p.	p_{PH_3}.	Δp_{PH_3}.	p.	p_{PH_3}.	Δp_{PH_3}.	p.	p_{PH_3}.	Δp_{PH_3}.	p.	p_{PH_3}.	Δp_{PH_3}.
0	0·490	0·114	—	0·576	0·200	—	1·154	0·782	—	0·768	0·397	—
1	0·432	0·084	0·030	0·451	0·105	0·095	1·099	0·704	0·078	0·653	0·298	0·099
2	0·397	0·058	0·066	0·384	0·057	0·143	1·050	0·653	0·129	0·596	0·244	0·153
4	0·350	0·034	0·080	0·331	0·017	0·183	1·005	0·572	0·210	0·543	0·189	0·208
8	0·326	0·021	0·093	—	—	—	0·961	0·468	0·314	0·495	0·132	0·265

These data are plotted in Figs. 1 and 2. In the former, the initial rate (R), the initial rate minus the rate of decomposition of phosphine ($R - R_0$), and the quantity $1/\tau - 1/\tau_0$ (τ is the time required for Δp_{PH_3} to reach 1·0 mm. and τ_0 that for the decomposition) are plotted against p_{O_2}. The three methods of plotting the results give closely parallel curves and it may be concluded that the order with respect to the oxygen pressure is two, since on plotting $1/\tau - 1/\tau_0$ against $p_{O_2}^2$, the line obtained is straight. Inspection of Fig. 2, where Δp_{PH_3} is plotted against time for three different pressures of phosphine, shows that the order is nearly zero. Unfortunately, the kinetics cannot be extended to higher pressures owing to explosion.

During these experiments, it was observed that a faint glow accompanied their progress. There was thus an indication that part of the reaction was homogeneous. In Table V, therefore, three runs are given using the same pressures of phosphine and of oxygen; in Expt. 201, argon was present from the start, in Expt. 202 it was added after 3 mins.; Expt. 203 is a run without argon. In all cases, as the decrease in the pressure of phosphine shows, there is no change in rate, and therefore an appreciable portion of the present reaction cannot be a chain process, since argon does accelerate the photochemical oxidation (Melville, *Proc. Roy. Soc.*, 1932, *A*, **138**, 389) below the lower limit.

Experiments were also made at total pressures of the order of 0·1 mm., but again no acceleration by inert gas could be observed. The homogeneous reaction which is responsible for the appearance of the glow can only form a very small part of the total. This is consistent with the fact that the intensity of the glow is even less than that in the oxidation of phosphorus, where the rate of oxidation was about 0·1 of that obtaining in the present experiments.

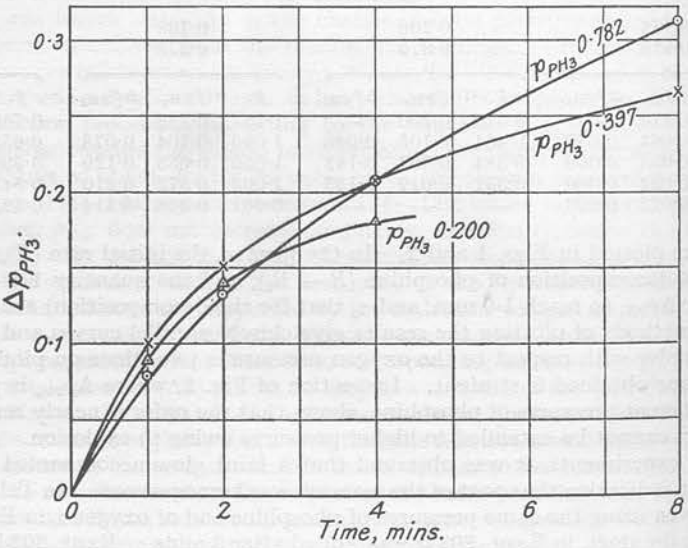
FIG. 1.



Broken line: graph of $1/\tau - 1/\tau_0$ *against* $p_{O_2}^2$.

Temperature coefficient. In order to ensure an accurate comparison, the apparent energies of activation (E) of the oxidation and decomposition were measured with the same specimen of wire, the one immediately after the other. The results are in Table VI, T being the absolute temperature.

FIG. 2.



Tungsten Filament.—The above experiments show that oxygen does not displace adsorbed phosphine from a molybdenum surface, since the rate of reaction is almost independent of p_{PH_3}, thus agreeing with the data on the decomposition. With tungsten, however, the decomposition at pressures of the order of 1 mm. is unimolecular, and therefore it might be expected that the

TABLE V.

Molybdenum filament; temp. 836° K.

	Expt. 201.			Expt. 202.			Expt. 203.		
p_{PH_3}	0·409			0·424			0·424		
p_{O_2}	0·380			0·375			0·375		
p_A	0·512			0·603			—		
t.	$p_{tot.}$	p_{PH_3}.	Δp_{PH_3}.	$p_{tot.}$*	p_{PH_3}.	Δp_{PH_3}.	$p_{tot.}$	p_{PH_3}.	Δp_{PH_3}.
0	1·301	0·409	—	0·799	0·424	—	0·799	0·424	—
1	1·204	0·303	0·106	0·689	0·327	0·097	0·693	0·330	0·094
2	1·127	0·252	0·157	0·635	0·277	0·147	0·632	0·274	0·150
3	—	—	—	0·606	0·248	0·176	0·596	0·241	0·183
4	1·082	0·208	0·201	0·588	0·210	0·214	0·579	0·220	0·204
5	—	—	—	0·566	0·203	0·231	0·563	0·199	0·225
7	—	—	—	0·547	0·169	0·255	0·547	0·178	0·246
8	1·033	0·158	0·251	—	—	—	—	—	—

* $p_{tot.}$ does not include the pressure of the argon.

TABLE VI.

Expt. No.	p_{PH_3}.	p_{O_2}.	*T*.	$\log_{10}T_{1/4}$.	$\log_{10}T_{1/2}$.	*E* (kg.-cal.).
286	0·412	0·426	720°	1·699	—	35·8
285	0·426	0·416	691	0·230	—	
284	0·424	0·402	665	0·591	—	
287	0·417	0·439	651	0·699	—	
288	0·420	—	878	—	0·231	23·8
289	0·420	—	836	—	0·505	
290	0·420	—	793	—	0·820	
291	0·420	—	758	—	1·159	

$T_{1/4}$ is the time for 25% reaction, *i.e.*, for the consumption of 25% of the PH_3; $T_{1/2}$ is that for 50% reaction.

total order of the oxidation reaction would be 2 if the oxygen is not strongly adsorbed. The variation in rate with p_{PH_3} and p_{O_2} is given by the data in Table VII; the method of gas analysis was exactly the same as that adopted with molybdenum, including the glowing of the filament between the runs in order to obtain reproducible results.

TABLE VII.

Tungsten filament; temp. 768° K.

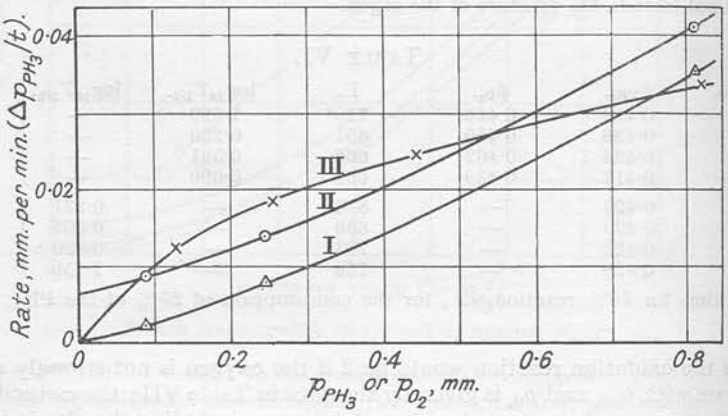
	Expt. 221. p_{PH_3}, 0·404; p_{O_2}, 0·411.				Expt. 222. p_{PH_3}, 0·403; p_{O_2}, 0·245.				Expt. 223. p_{PH_3}, 0·403; p_{O_2}, 0·084.			
t.	*p*.	Δp.	p_{PH_3}.	Δp_{PH_3}.	*p*.	Δp.	p_{PH_3}.	Δp_{PH_3}.	*p*.	Δp.	p_{PH_3}.	Δp_{PH_3}.
0	0·815	—	0·404	—	0·648	—	0·403	—	0·487	—	0·403	—
1	0·780	0·035	0·381	0·023	0·626	0·022	0·388	0·015	—	—	—	—
2	0·739	0·076	0·352	0·052	0·603	0·045	0·367	0·036	0·477	0·010	0·883	0·020
4	0·689	0·126	0·323	0·081	0·569	0·079	0·337	0·066	0·470	0·017	0·363	0·040
8	0·617	0·198	0·272	0·132	0·526	0·122	0·297	0·106	0·461	0·026	0·333	0·070
	Expt. 224. p_{PH_3}, 0·413; p_{O_2}, 0·819.				Expt. 227. p_{PH_3}, 0·127; p_{O_2}, 0·412.				Expt. 228. p_{PH_3}, 0·262; p_{O_2}, 0·411.			
0	1·232	—	0·413	—	0·539	—	0·127	—	0·673	—	0·262	—
1	1·163	0·069	0·371	0·042	—	—	—	—	0·636	0·037	0·254	0·008
2	—	—	—	—	0·483	0·056	0·101	0·026	0·607	0·066	0·223	0·039
4	1·020	0·212	0·269	0·144	0·449	0·090	0·081	0·046	0·564	0·107	0·190	0·072
8	0·892	0·340	0·184	0·229	0·398	0·141	0·051	0·076	0·506	0·167	0·147	0·115
	Expt. 230. p_{PH_3}, 0·812; p_{O_2}, 0·398.				Expt. 225. p_{PH_3}, 0·420; p_{O_2}, —.							
0	1·210	—	0·812	—	0·420	—						
1	1·190	0·020	0·786	0·026	—	—						
2	1·159	0·051	0·737	0·075	0·407	0·013						
4	1·123	0·087	0·712	0·100	0·398	0·022						
8	1·061	0·149	0·649	0·163	0·368	0·052						

The data of Table VII are plotted in Fig. 3. Curve I is the R–p_{O_2} graph, and II the (R – p_{O_2} graph. The rate is nearly proportional to p_{O_2}, contrasted with the bimolecular course for molybdenum. Curve III is for various phosphine pressures, and here the order is less than unity, since the initial increase in R is not maintained, but gradually falls off. If log R be plotted against log p_{PH_3}, the slope of the line is 0·5, and therefore $R \approx p_{PH_3}^{1/2}$.

The effect of argon was also investigated, to see if there was any measurable chain reaction as a faint glow was observed in these experiments. Again, however, no acceleration could be detected, so that the reaction must occur almost entirely on the surface. The pressures employed were 0·4 mm. of phosphine and of oxygen and 0·5 mm. of argon.

Temperature coefficient. In Table VIII, data are given for the oxidation and decomposition at a number of different temperatures. It will be observed that although the rate of oxidation is not much faster than the decomposition, yet the fact that the pressure of non-condensable gas ($p_{tot.} - p_{PH_3}$) decreases a little, shows quite definitely that there is very little decomposition accompanying oxidation.

FIG. 3.



Two further efforts were made to induce the initiation of chains. A silica and also a Pyrex filament replaced the tungsten one, but although the rate of oxidation was greater than that of the decomposition, no acceleration by argon was observed. Finally, owing to the fact that phosphine raises the lower oxidation limit of explosion of phosphorus–oxygen mixtures (Melville, *Trans. Faraday Soc.*, 1932, **28**, 314), phosphorus vapour was added to phosphine–oxygen mixtures in the hope that, since a reaction occurs on the surface which leads to the evaporation of a molecule capable of starting the phosphorus–oxygen chains, the same molecule might provide centres for the phosphine reaction. There was, however, no acceleration of the reaction; indeed, a slight retardation was found. The pressure of phosphorus vapour did not exceed 0·030 mm.

TABLE VIII.

(D = Decomposition; O = oxidation; E_D = 24·3 kg.-cals.; E_O = 21·8 kg.-cals.)

Temp., K.	931°.	879°.			833°.			768°.		
	D.	D.	O.		D.	O.		D.	O.	
t.	p_{PH_3}.	p_{PH_3}.	$p_{tot.}$.	p_{PH_3}.	p_{PH_3}.	$p_{tot.}$.	p_{PH_3}.	p_{PH_3}.	$p_{tot.}$.	p_{PH_3}.
0	0·399	0·401	0·794	0·399	0·400	0·795	0·399	0·404	0·788	0·397
1	0·328	0·328	0·699	0·310	0·370	0·716	0·332	—	0·755	0·371
2	0·263	0·263	0·621	0·239	—	0·659	0·279	0·398	0·726	0·351
4	0·158	0·273	0·527	0·153	0·313	0·576	0·201	0·382	0·672	0·303
8	—	0·174	—	—	0·251	0·467	0·092	0·362	0·592	0·230

Temp., K.	730°.			698°.	
	D.	O.		O.	
t.	p_{PH_3}.	$p_{tot.}$.	p_{PH_3}.	$p_{tot.}$.	p_{PH_3}.
0	0·395	0·804	0·412	0·795	0·401
2	—	0·775	0·401	0·774	0·382
4	0·385	0·749	0·381	0·756	0·371
8	0·375	0·719	0·352	0·731	0·357
16	0·361	0·657	0·310	0·690	0·325

A peculiar observation with regard to the deposition of red phosphorus was made after a number of oxidation experiments had been carried out. The walls of the reaction tube opposite the filament were covered by a fairly uniform layer of HPO_2. When phosphine was decomposed on the filament, the red phosphorus was not deposited on top of the acid film but at the extreme ends of the tube, where there was little HPO_2. The phosphorus molecules (P_2 as suggested before) are apparently efficiently reflected from an HPO_2 surface but are relatively easily condensable on a silica surface.

Discussion.

Since the orders of the decomposition and oxidation of phosphine on molybdenum with respect to the phosphine pressure are nearly the same in the pressure region where comparison may be made, it would appear that oxygen is unable to displace adsorbed phosphine. Oxidation, then, probably occurs by the impact of molecular oxygen on a phosphine-covered filament. When the oxygen pressure is equal to or less than that of the phosphine, and where analysis of the gas mixtures indicates the production of HPO_2, the simplest mechanism which may be postulated is the following: Phosphine is decomposed step by step on the molybdenum surface, $Mo - PH_3 \longrightarrow Mo - PH_2 \longrightarrow Mo - PH \longrightarrow Mo - P$, the PH_2, PH, or P remaining strongly adsorbed until there is reaction between adjacent radicals to yield P_2 and H_2, which evaporate. During the progress of this series of reactions, an oxygen molecule may collide with a PH radical to form HPO_2. If the oxygen pressure is very small, the probability of reaction is so small that most of the phosphine is decomposed directly into its elements; on the other hand, if this pressure is large, the phosphine would seem to be attacked before the intermediate steps in its decomposition take place, for the decrease in pressure of non-condensable gas points to the production of a highly oxidised molecule such as phosphoric acid. It may be that it will then be necessary for two oxygen molecules to collide in close proximity to one phosphine molecule in order to effect this oxidation, in which case the reason for the bimolecular nature of oxidation would become clear. Why the reaction should follow a bimolecular course when only HPO_2 is formed is not, however, obvious.

A somewhat similar mechanism would also apply to the reaction on tungsten filaments; but there are deviations; for example, the order of the reaction with respect to phosphine pressure is not unity as in the decomposition experiments. This is possibly due to the fact that since phosphine is not so strongly adsorbed on tungsten as on molybdenum, oxygen is able to hinder the increased degree of adsorption necessary to maintain unimolecular characteristics. With tungsten, therefore, the oxidation probably occurs by the interaction of adsorbed phosphine or its intermediate products of dissociation and oxygen adsorbed on the metal surface.

In spite of these two slightly different methods of oxidation, the possibility of the evaporation of a molecule capable of starting a chain in the gas phase must be very small. Even when p_{O_2} is much less than p_{PH_3} and there is a chance of the evaporation of P_2 molecules, there is no homogeneous reaction. The experiments with phosphorus vapour likewise indicate that the carriers in the phosphorus reaction cannot induce reaction in phosphine–oxygen mixtures. In this case, of course, the ejection of carriers may be interfered with by phosphine itself. Some such action is not altogether unexpected in view of the fact that phosphine has the unique property of raising the lower explosion limit of phosphorus vapour. Another point emerges from these experiments; HPO_2 molecules when evaporated from a hot filament are incapable of reacting with oxygen to yield suitable chain carriers. The difference in the phosphine and phosphorus reactions must therefore be due to the behaviour of these molecules on the surface of the catalyst. In the former, the intermediate products of dissociation, which are undoubtedly reactive and suitable for chain propagation, as is shown by the photochemical experiments, are so strongly adsorbed to the metal surface that they are unable to evaporate before attack by oxygen. The faint glow that is observed may be due to a very small fraction of these being able to escape from the surface. In the latter reaction, on the other hand, the only intermediate product is probably P_2 (the filament is hardly hot enough for phosphorus atoms to be present in any quantity; compare Preuner and Brockmoller, *Z. physikal. Chem.*, 1913, **81**, 159), which can

be easily and quickly desorbed from the surface before the arrival of oxygen molec On a platinum filament, where the reaction takes place wholly on the surface, the fact the rate is of zero order with respect to the concentration of phosphorus vapour, shows adsorption is very strong. An oxygen molecule has therefore a good opportunity reacting with adsorbed phosphorus.

It has been shown (Fig. 3) that the rate of oxidation on molybdenum is somewhat than the decomposition at 836° K. If, however, the velocity measurements could extended to a much wider range, it would be observed, since $E_O > E_D$, that (*a*) at temp atures higher than 836° K., the rate of oxidation would become very much greater than decomposition, (*b*) at temperatures less than 836° K., the decomposition would become preponderant reaction and the oxygen would be without effect. It is remarkable that tungsten $E_O \doteqdot E_D$.

The Effect of Atomic Hydrogen on the Catalytic Decomposition of Phosphine and Ammon

In the photochemical experiments on the decomposition of phosphine, it was show that atomic hydrogen can react with the transitory intermediate products of the dis sociated molecule to re-form phosphine; similar effects were obtained with ammon (Melville, *Trans. Faraday Soc.*, 1932, **28**, 885).* It was suggested that the inhibition wa due to the reaction $H + PH_2(NH_2) \longrightarrow PH_3(NH_3)$, occurring at the walls of the reaction tube. If the decomposition of these molecules on the surface of a filament takes place stages with the production of surface compounds of the nature $W–PH_2$ or $W–PH$, then it should be possible, in principle, to bombard the filament upon which phosphine or ammonia is being dissociated and so retard the rate of decomposition. The result of such an experiment is a little difficult to interpret for phosphine since there is the possibility of the reduction of the phosphorus in the gas or at the walls before condensation to the red modification.

The experimental procedure was similar to that employed in the photochemical experiments, the atomic hydrogen being produced by collision of the gas with an optically excited mercury atom. The reaction tube in Fig. 1 of the first paper (*loc. cit.*) was replaced by one of silica 2·5 cm. in diameter, whilst the filament assembly remained the same. It was not possible to use the oil manometer with ammonia as this gas dissolved very rapidly in the oil; nor could nickel be used for phosphine owing to disintegration of the filament.

TABLE IX.

Gas.	Filament and conditions.*	Time of expt.	p_X.†	p_{H_2}.	Δp_X.	Gas.	Filament and conditions.*	Time of expt.	p_X.†	p_{H_2}.	Δp_X.
PH_3	Mo; *L*	5	0·286	0·636	0·124	PH_3	W; *L*	2	1·84	3·66	0·87
	L+*F*	5	0·292	0·636	0·189						(0·98)
					(0·472)		*F*	2	1·91	3·59	0·09
	F	5	0·295	0·633	0·248		*F*+*L*	2	1·96	3·60	0·84
NH_3	Mo; *F*	2	2·06	4·06	1·44	NH_3	Ni; *F*	2	1·87	3·74	0·29
	L	2	1·83	4·20	0·00		*F*+*L*	2	1·95	3·57	0·15
	L+*F*	2	1·83	4·20	0·90		*L*	2	1·95	3·57	0·00
PH_3	Mo; *F*	2	1·92	5·58	1·62	PH_3	W; *L*+*F*	4	0·278	0·582	0·153
	F+*L*	2	1·92	5·38	1·14						(0·234)
					(1·69)		*L*	4	0·298	0·580	0·045
	L	2	1·77	5·88	0·07		*F*	4	0·283	0·582	0·186
NH_3	W; *L*	2	1·93	4·02	0·01		*L*	4	0·308	—	0·111
	F	2	1·55	3·93	0·78						
	F+*L*	2	1·91	3·72	0·56						
					(0·79)						

* *L* = Lamp, *F* = filament. The figures in parentheses refer to the amount of gas decomposed by the lamp and the filament when used separately. † $p_X = p_{NH_3}$ or p_{PH_3}.

An inspection of the results (Table IX) shows that in every case the amount of gas decomposed by the filament and lamp simultaneously is less than that when these agents are

* The results with ammonia have been confirmed and extended by Dr. L. Farkas, using the velocity of the change $H_{2(para)} \longrightarrow H_{2(ortho)}$ to measure the concentration of atomic hydrogen (private communication).

erated separately; *i.e.*, the simultaneous production of atomic hydrogen with the dissociation of ammonia or phosphine leads to a retardation of the latter process. This result almost to be expected for ammonia, as molecular hydrogen is an inhibitor for the decomposition. The dissociation of hydrogen no doubt facilitates adsorption, for it virtually removes the necessity of activation which is required when a normal hydrogen molecule collides with the catalyst. The inhibition must occur on the surface of the wire since atomic hydrogen does not attack molecular nitrogen in the gas phase. The hydrogen atoms probably react with the surface compounds, M–NH or $M–NH_2$, which are formed during the decomposition (Frankenburger and Hodler, *Trans. Faraday Soc.*, 1932, **28**, 229, and subsequent papers in *Z. Elektrochem.*).

That a similar mechanism holds for phosphine is probable from the following argument. If a mixture of phosphorus and mercury vapours is illuminated by a mercury lamp, there is a deposition of red phosphorus. The P_4 molecules are therefore changed in some way so that they undergo the allotropic transformation. If hydrogen is present also, no appreciable amount of phosphine is produced, *i.e.*, atomic hydrogen does not attack these reactive molecules derived from P_4. If the same molecules give rise to the red phosphorus in the thermal decomposition experiments, then it is improbable that atomic hydrogen can react to yield phosphine. The retardation observed is therefore likely to have taken place on the surface of the filament itself, as in the ammonia reaction. It is surprising, in view of the similarity in the behaviour of atomic hydrogen with respect to ammonia and phosphine, that in the latter case inhibition by molecular hydrogen is absent.

Summary.

The kinetics of the oxidation of phosphine on molybdenum and tungsten filaments at pressures below the lower explosion limit have been investigated in order to determine whether a hot filament might induce the homogeneous combination of the gases, as is the case with phosphorus–oxygen mixtures. No measurable amount of homogeneous reaction could be detected, the reaction taking place almost wholly on the surface; a faint glow accompanied the oxidation, however, thus providing evidence of a trace of homogeneous reaction. Experiments with a silica and with a Pyrex filament were also unsuccessful. The presence of phosphorus does not induce the reaction to come off the surface.

A theory is proposed to account for the differences in the reactions of oxygen with phosphine and with phosphorus.

Experiments are described in which the catalytic decomposition of phosphine and ammonia is inhibited by the simultaneous bombardment of the filament by atomic hydrogen.

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DISCUSSION ON ENERGY DISTRIBUTION IN MOLECULES IN RELATION TO CHEMICAL REACTIONS

Opening Address by

C. N. Hinshelwood, F.R.S.

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Discussion on Energy Distribution in Molecules in Relation to Chemical Reactions

Opening Address

By C. N. HINSHELWOOD, F.R.S.

(May 10th, 1934)

It often happens that the empirical observations of chemistry reveal the working of principles which can be easily interpreted in terms of physical theories, but which might have been difficult to predict. One need only mention the question of the nature of valency as one of the most conspicuous examples. For this reason it is useful if problems lying on the border line of physics and chemistry are discussed from both points of view.

The present theme is the distribution of energy in molecules and its relation to the phenomena of chemical change. We know that the transference of energy from one molecule to another and, in particular, the accompanying interconversion of translational and internal energy depend upon specific mechanisms which give rise to phenomena of great interest. I need only mention the influence of hydrogen and certain other gases in maintaining the energy distribution in unimolecular reactions, the variation of the velocity of sound with frequency, due to the finite time required for the establishment of equilibrium in the energy distribution among the internal degrees of freedom, and lastly that curious inability of solvent molecules to degrade the light energy absorbed by fluorescent substances.

There are still interesting things to be known about these phenomena, especially on the theoretical side, but I will pass on to some newer problems connected with internal rearrangements of energy which has already been given to a molecule. As we know, one form of this problem has been very prominent of late years in connexion with the type of photochemical decomposition called predissociation.

The first of the chemical problems to which I should like to draw attention is connected with the existence of what we may call independent modes of activation of the molecules taking part in certain reactions. The experimental facts are as follows. If, for a reaction involving the decomposition of a single substance, we plot the reciprocal of the time of half change against the initial pressure we obtain, in general, a curve which first rises and then bends round

to become parallel to the pressure axis. The interpretation of this curve in terms of the activation and deactivation of molecules by collision, and the transformation probability of the activated molecule is well known. Now in certain cases there is clear evidence that the curve is really composed of the superposition of several curves, and does in fact present a well-defined segmented appearance. The interpretation which we have tentatively given to this is that there are several virtually independent reactions taking place at the same time, all unimolecular, and differing only in the values of the various characteristic constants. This type of behaviour is found with nitrous oxide, with acetaldehyde and with propionic aldehyde. With the two former substances at any rate, the chemical nature of the reaction is essentially the same over the whole pressure range, so that we appear to have several physically different mechanisms by which molecules are activated for the same unimolecular chemical transformation. The hypothesis which we have found most useful in explaining this is that once a molecule has received its activation energy, the internal rearrangement of this energy is relatively difficult, and that according to the original way in which the energy was placed in the molecule there will be a different probability of chemical decomposition. To illustrate the point with one very rough example, if the N-N link of nitrous oxide is activated to a high vibrational level the probability of the decomposition $N_2O = N_2 + O$ will clearly not be the same as when the N-O link is activated. Thus the N-N activated molecules and the N-O activated molecules will undergo what are virtually independent reactions. This is an unduly simplified picture, no doubt, of what constitutes one of these modes of activation. In the hope of throwing further light on this, we have recently been making a comparison of the kinetic behaviour of a series of related compounds to see how the prominence of a given mode varied with the presence of a substituent. The series chosen was HCHO, CH_3CHO, C_2H_5CHO and CCl_3CHO. I will not describe the experimental results in detail here. They form the subject of a paper now in the hands of the Royal Society, and my colleague, Mr. Fletcher, will say something about them in the course of this discussion. But I will summarize certain conclusions upon which the views of theoretical physicists would be helpful. These are (*a*) the hypothesis that molecules with the activation energy differently located or distributed do seem frequently, and perhaps generally to behave as virtually independent entities for kinetic purposes appears to be confirmed; (*b*) that, in certain substances at least, although several types of activated molecule are detectable, the number is not indefinitely great, or at any rate the types fall into a few well-differentiated

groups; (*c*) in a molecule like HCHO the chance that the activation energy is communicated to the molecule in such a way as to cause rapid decomposition is relatively much greater than with substituted molecules such as C_2H_5CHO; (*d*) with CCl_3CHO, the CCl_3 part of the molecule is much more likely to be activated than the CHO part. To what extent this is simply a function of the greater mass of the chlorine atoms is an interesting question; (*e*) from the purely experimental point of view we are not yet able to estimate the relative importance of "valency oscillations" and "deformation oscillations" of the molecule, though on general grounds the importance of the latter appears to be considerable.

The question of the relation between the actual magnitude of the activation energy and the decomposition probability raises interesting questions which, however, cannot be dealt with here, as we must pass on to other matters.

The next group of problems coming within the scope of this discussion I will only just mention. In a large class of reactions it may be ambiguous whether a decomposition occurs by the mechanism $XY_2 = X + Y_2$, or by the alternative $XY_2 = XY + Y$, and subsequent reaction of the active radicle Y. I hope there may be some discussion of the general aspects of this problem, and will only say that in my opinion the dissociation idea is often carried too far, and that frequently interaction between two parts of a molecule is a process occurring more easily than the development of either in a free state.

I will now turn to a rather different type of problem, where transition probabilities of activated molecules are concerned even more intimately. There is a large class of bimolecular reactions in solution where the observed rate is as nearly as may be equal to the rate of encounter of the appropriate activated molecules. There is a second class where the reaction velocity is many powers of ten smaller than the activation rate. (Doubtless there is a continuous transition between the two classes, but we may consider extreme examples. Reactions of the second class are very sensitive to the catalytic action of solvents, and it thus appears probable that a ternary collision involving a solvent molecule is necessary. In one example, namely, the benzoylation of amines in organic solvents Mr. E. G. Williams and I have been able to show that even when the condition of a simultaneous collision between two reactant molecules, suitably activated, and a solvent molecule is fulfilled, the transformation probability is still small. I have suggested that perhaps we ought to distinguish two extreme cases in chemical kinetics; the first where the rate of reaction is primarily determined by the acquisition of the necessary activation energy, and the second where a probability factor independent of temperature is of

equal or greater importance. Such a factor would be characteristic of a problem in which a quantum mechanically "forbidden" transition was involved. Such transitions occur when certain types of electronic reorganization are involved. They are greatly facilitated by perturbing forces acting on the molecules. There is a suggestive connexion between this and the remarkable catalytic effect of solvents—often roughly parallel with their polarity—on the one hand and, on the other hand, with the fact that in reactions where one of the reactants is an ion the rate is usually nearly equal to the activation rate, as though the great electrostatic forces contributed a perturbation powerful enough to increase the transformation probability to nearly unity.

(*Slides illustrating experimental results were shown.*)

Professor J. E. Lennard-Jones, F.R.S.—It seems to me that there is no branch of chemistry in which it is more important to understand, in a detailed way, the electronic structure of molecules than in the branch under discussion to-day. One of the methods which have been used to determine electron distribution in molecules starts from the assumption that each electron may be regarded as moving independently in the field of the complete nuclear framework. The properties of the various possible states are then determined by the symmetry of the environment in which the electrons move. Some of these states have the same symmetry of the nuclear framework, and may be regarded as symmetrically (though not equally) related to all the nuclei, while others have different symmetry properties and indicate that electrons in those states prefer to avoid certain parts of the molecule (as, for instance, certain planes of symmetry). When one electron of a molecule is excited by light absorption (or other means) from a state which is of the symmetrical type to one of unsymmetrical type, some of the bonds of the molecule are affected to a greater extent than the rest. The effect may sometimes be so drastic as to cause the molecule to dissociate at a particular link or to cause a rearrangement of the valency links.

It is believed that molecules which dissociate in unimolecular reactions do so without light absorption. None the less, a transition may occur from one electronic state to another, if the vibrational energy is such that the nuclei of the molecule can take up certain special configurations. It is, therefore, of importance to know the energy of the various states of the molecule for all possible configurations of the nuclear framework.

Mr. Hinshelwood, in his opening address, has referred to the mechanism of the decomposition of molecules of the type AB_2. At present it is not yet known whether these molecules decompose into $A + B_2$ or into $AB + B$, or what the factors are which control the products of decomposition. In this connection I may refer to some recent work of mine on the electronic structure of certain molecules of this type for it may suggest the mechanism, by which these molecules decompose. If the molecule AB_2 has the symmetry of the letter Y, the electronic orbitals are of three types. They may most easily be described by reference to three rectangular axes, of which the axis of z is along the axis of the molecule, while the axes of x and y are respectively perpendicular to and parallel to the plane containing the nuclei.

One kind of molecular orbital has the same symmetry as the nuclear framework so that it is unaffected by reflection in the planes xy and yz. This is called an "a_1" orbital. Another kind is such that the wave function vanishes everywhere in the yz plane, so that reflection of the wave function in the plane causes a change of sign. This is called a "b_1" orbital. The third type has a nodal plane in the xz plane. This is called a "b_2" orbital. There are, of course, many orbitals of each type, just as there are many s- and p-orbitals in atoms, each having its characteristic quantum number or nodal surfaces, but all orbitals conform to one of the three types just described.

The wave function of the *whole* electron distribution may be described in an analogous way. It may have a symmetry of the same type as an individual orbital, which we have labelled "a_1." It is then described as an "A_1" state. Similarly there are B_1 and B_2 states.*

The electronic structure of formaldehyde, acetone, and certain other ketones can be described in terms of this notation. I have recently made a study of the electronic states of formaldehyde by correlating them with those of the oxygen molecule, which contains the same number of electrons. It appears that among the low energy levels there are three transitions from the ground state ^1A, one to another $^1A_1$ level, one to a $^1B_2$ level and one to a $^1B_1$ level. In the first transition the symmetry of the molecule does not change, while in the second ($^1A_1$—$^1B_2$) and third ($^1A_1$—$^1B_1$) the symmetry changes in such a way as to correspond to a change of the electric moment in the direction of the y-axis, and x-axis respectively.

Now Dieke and Kistiakowsky† have recently shown that the characteristic

* For reasons into which I need not enter, there is also another state labelled A_2.

† 'Phys. Rev.,' vol. 45, p. 4 (1934). I am indebted to Dr. Snow for bringing this reference to my notice and for interesting discussions on this subject.

absorption band of the CO group in formaldehyde in the neighbourhood of 3000 A does in fact correspond to a change of moment parallel to the y-axis, and we may, accordingly, infer with some degree of certainty that absorption in this region of the spectrum corresponds to the $^1A_1 \longrightarrow {}^1B_2$ transition. Presumably the characteristic absorption of aldehydes, ketones and all other molecules containing a CO group in the region of 3000 A corresponds to a transition of this type.

When the detailed electron structure appropriate to each of these states is examined, it is found that the ground state has its two outermost (or most lightly bound) electrons in b_2 orbitals, viz. $(b_2)^2$, while the corresponding electrons in the $^1B_2$ excited state are (b_2) and (a_1), one of the electrons having been lifted from a b_2 orbital to an a_1 orbital. This means that the electron distribution has altered in such a way as to throw the H-atoms into a closer relation to each other. It would not be surprising, therefore, if the molecule subject to light in the region of 3000 A dissociated according to the scheme

$$H_2CO \longrightarrow H_2 + CO.$$

I understand that Dr. Norrish has obtained experimental evidence of the decomposition of molecules of this type when subject to radiation of this wave-length.

There may, however, be a difference between the case of formaldehyde and that of other Y-shaped molecules such as acetone, because the H-atoms are in a sense spherically symmetrical and can react with each other whatever their relative orientation, whereas two CH_3 groups can only react to form ethane provided the two groups are oriented in a particular way. Hence it is possible that aldehydes R . CHO and ketones R . R'CO may dissociate in different ways. This suggests the necessity of a theoretical investigation of the electronic states of these various molecules and their energies as functions of the internuclear distances.

Even when the energies of the various states of a molecule are known as functions of the internuclear distances (or other suitable parameters), there still remains the difficulty of representing the results in a graphical way so as to facilitate comparison of experimental and theoretical results. One reason why so much progress has been made with diatomic molecules is that energy diagrams are functions of one co-ordinate and can conveniently be represented in a two-dimensional space. The usual method of representing the energies of molecules with two degrees of freedom is by a system of equipotential curves in a two-dimensional space. Each energy state requires one complete

system of curves, so that when a number of such sets of curves are superimposed, the network is so complicated as to be useless. The next method is to represent the energy of each state by a surface, the height of each point above a plane representing the energy appropriate to that molecular configuration. This is most helpful when only one state, say the ground state of a molecule, is being considered. When several states have to be considered simultaneously, it is again impossible, in practice, to construct a number of intersecting surfaces without causing great confusion. Moreover, it is difficult to commit the results of such an analysis to paper.

In order to overcome these difficulties I have found it advantangeous for molecules where two degrees of freedom are important, to use the following method. Let x and y be the co-ordinates associated with the two degrees of freedom in which we are most interested. We suppose them measured as usual along two perpendicular directions, and the energy appropriate to any configuration (x, y) is represented by an ordinate (z) perpendicular to the plane xy. In problems of photochemistry interest is usually centred in the possible transitions from a particular state of the molecule (say the ground state) and by the Franck-Condon principle the transitions mostly take place from the neighbourhood of the minimum of the energy surface, whose co-ordinates are $(x_0 y_0)$. It, therefore, seems advantageous to concentrate on the transitions from this neighbourhood and to take a section $x = x_0$ and $y = y_0$ through all other energy surfaces. If, in addition, the parameters are chosen in such a way that all possible configurations of the molecule are represented by a finite range of values of x and y, say from $(x_0 y_0)$ to (x_1, y_1), then the energy surfaces can conveniently be represented by their sections on a foursided blackboard made in the form of a cylinder of square cross-section.

If, for example, a linear molecule ABC is being considered, then, as long as it is linear, it can be described by two distances, which may describe the length of the link AB and the length of the link BC. Then one side of the blackboard will represent the interaction of A and B when C is at an infinite distance from both. This interaction may be denoted by $(A \longleftrightarrow B) + (C)$. The other three sides will represent the interactions

$$(AB \longleftrightarrow C, \qquad A \longleftrightarrow (BC) \qquad \text{and} \qquad A + (B \longleftrightarrow C).$$

An example of a scheme of energy levels for a molecule of this kind is shown in fig. 1. Another method of representing the same set of surfaces is given in fig. 2, where the curves appearing on the four sides of the four-sided blackboard are drawn in four panels in the same plane.

A similar method of representation can be used for a Y-shaped molecule like formaldehyde, if we suppose the CO part of the molecule to remain fixed and the hydrogens to approach and recede from the molecule symmetrically, that is, so as to preserve the symmetry of the Y. Then the distance of the mid-point of the line joining the two H-atoms from the carbon atom can be

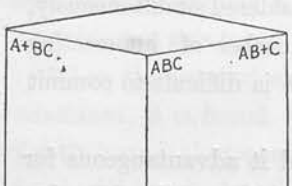


FIG. 1

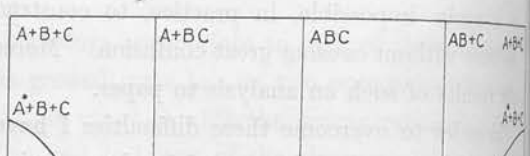


FIG. 2

taken as one co-ordinate (x), and the distance between the H-atoms as the other (y). For molecules of this kind the symbolic representation of the energy levels is of the type shown in fig. 3. Denoting the molecule by XR_2, the first panel shows the interaction of R and R at an infinite distance from X.

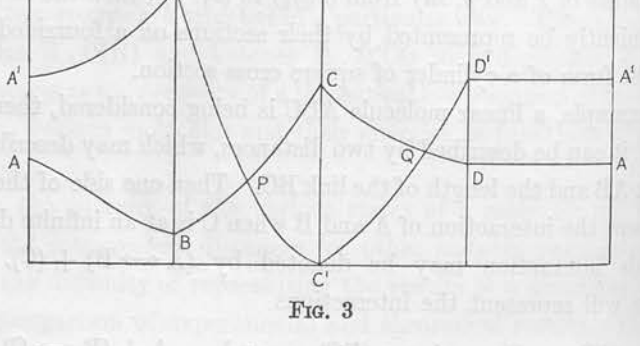


FIG. 3

The second shows the interaction of, R_2 and X when the R_2 molecule is brought towards X in such a way that its mid-point moves along the axis of symmetry of X and the correct symmetry of the XR_2 system is preserved; in this process, the internuclear distance of the atoms of R_2 is kept fixed. In the third panel the interaction of R_2 and X is shown where the R atoms are drawn apart

from each other in such a way that their centre of gravity remains fixed at the equilibrium distance from X, and the symmetry of the system X + R + R is preserved. In the last stage the R atoms, already at an infinite distance from each other, are moved so that their centre of gravity recedes from X. During this process the energy does not change but the cycle is completed and the system returned to its original configuration.

In the figure two energy surfaces are represented by the curves ABCDA and A′B′C′D′A′ and their *curve* of intersection by two *points* P and Q. The point C′ represents the minimum of the energy surface and the vibrations of the molecule at low temperatures can be represented by the movement of a point about C′.

If, as a result of collision, the molecule receives sufficient energy to reach the point P, an electronic transition may occur, provided that the intersecting surfaces correspond to states of the same symmetry and the same multiplicity (that is, the same spin vector). The molecule will then decompose into $X + R_2$. Similarly if the molecule receives sufficient vibrational energy to reach the point Q, the molecule will decompose into X + R + R. (In order to consider the possibility XR + R, a third co-ordinate and therefore a more complex energy diagram would be necessary.) The curve of intersection, of which P and Q are two points, will in general be non-planar and will resemble a rim which has become warped. It will have two minima such as P and Q (not usually at the same height) and two maxima in between them. In consequence, the probability of decomposition and the products of decomposition will depend on the energy. It will increase from zero as the vibrational energy increases from a certain critical value (corresponding to the height of P on the energy diagram) until it reaches a maximum, after which it may decrease again, for, when the vibrational energy of the molecule exceeds that of the highest point of the curve of intersection, the probability of a spontaneous switch from one surface to another will become small. The energy must therefore lie within definite limits for decomposition, which involves a switch between these two energy states.

The conditions for decomposition become more complex if the two energy surfaces correspond to states of different multiplicity. If, for example, the lower one is a $^1A_1$ state, in the notation already explained for a Y-shaped molecule, while the upper one (BCD) is a $^3A_1$ state, then a switch from one surface to another at P or Q will not always occur. The probability of transition will be very much smaller and may be of the order of 10^{-3} or less, just as transitions from a triplet to a singlet level in emission or absorption are

much less frequent than those between levels of the same multiplicity. The probability of decomposition under these conditions will therefore depend on two factors, viz., (i) the energy, which must lie within prescribed limits, and (ii) a change of spin of the electrons. The latter will be affected by the environment in which the molecule moves and may be accelerated by the presence of electric or magnetic fields. This may be the explanation of the effect of various solvents on decomposition, to which Mr. Hinshelwood has referred.

Professor M. Travers, F.R.S.—The following note is based upon the results of work carried out in the Chemical Laboratories of the University of Bristol conjointly with Dr. T. J. P. Pearce, Mr. R. V. Seddon, B.Sc., and Mr. P. F. Gay. The work involved the study of the pyrolysis of acetaldehyde, and also of ethane and ethylene, and the equilibrium mixtures of these gases with hydrogen. The work on the acetaldehyde is in progress, but the investigation of the hydrocarbons is completed, and will be communicated to the Society in the course of a few days.

It appears from the circular issued to the Fellows of the Society that the ideas which Mr. Hinshelwood proposes to put forward for discussion are based upon the results of a series of investigations, such as that carried out by himself and Mr. Hutchinson* on the pyrolysis of acetaldehyde. It is proposed to put forward some facts which show that the conclusions arrived at from this work may be open to serious question, and that the basis for the present discussion is by no means a sound one.

In the latter investigation the decomposition of acetaldehyde was supposed to proceed according to the equation,

$$C_2H_4O = CH_4 + CO,$$

side reactions being negligible. The rate of reaction was measured between 430° and 592° C, and at initial pressures below 479 mm, by first connecting an exhausted silica bulb with a vessel containing pure aldehyde at a known temperature for a moment, and then observing the rate of change of pressure. The half-life period was calculated from the results, and it was concluded that—

(i) the reaction was bimolecular;

(ii) it was practically homogeneous;

* 'Proc. Roy. Soc.,' A, vol. 111, p. 580 (1926).

(iii) it was entirely unaffected by the products of decomposition of the acetaldehyde; and

(iv) no carbon dioxide or unsaturated hydrocarbons were formed.

Using an entirely different method of investigation, we have arrived at conclusions which are generally the reverse of those stated above. Briefly, the method involved the accurate measurement of a volume of acetaldehyde, which was condensed in a silica reaction tube, cooled with liquid air, and then sealed. The tube was then heated for a definite period, and the contents were analysed for methane, carbon monoxide, carbon dioxide, aldehyde, propylene, and propane. The method was laborious but accurate. As some carbon monoxide was formed together with the propylene by a reaction which followed on a condensation process, the rate of formation of methane was taken as indicating the rate of the main reaction.

Now the graphs representing the rate of this main reaction are not continuous, so that the half-life period can have no real meaning. However, the initial portions are nearly linear, so that the initial rates can be determined graphically. It would now seem to be a simple matter to find the variation of the rate of reaction with temperature, but here we encounter another difficulty. The rates of reaction are influenced to a marked extent by the state of the surface.

These facts are well illustrated by the accompanying graphs. At 400° each point on the diagram represents the result of an experiment carried out after the reaction tube had remained heated to 600° overnight while full of hydrogen. At 380° two series of experiments were carried out, A in which the reaction tube was preheated overnight while filled with hydrogen, and B, in which the pretreatment with hydrogen lasted only 2 hours. From the experiments at 400° and series A at 380° the critical increment of the process was found to be 24·6 k. cals., and from the experiments at 400° and series B at 380° it was found to be 31·1 k. cals. Also, with different reaction tubes different rates of reaction were obtained at the same temperature. In silica apparatus, therefore, the process is not mainly homogeneous, but is materially influenced by surface conditions.

The process is very considerably accelerated by the addition of carbon monoxide, methane, or even of hydrogen, and to almost the same extent by any one of these gases. On increasing the quantity of either of the gases it is found that the rate of decomposition of the aldehyde reaches a maximum, and a further addition of the gas leads to a reduction in the apparent rate of

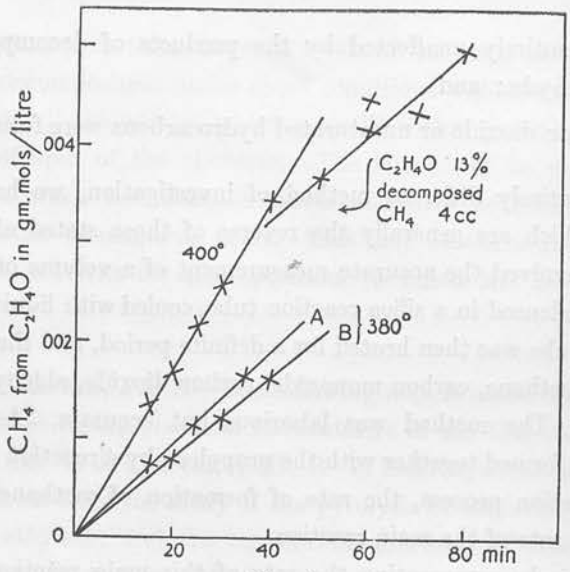


FIG. 4

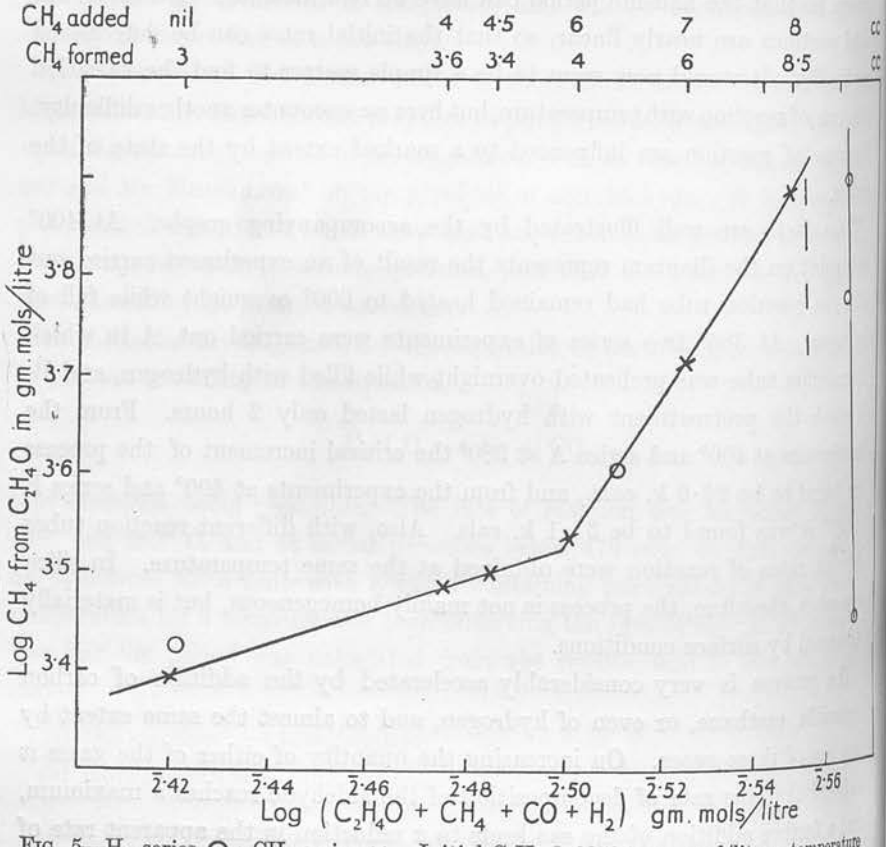


FIG. 5—H_2 series O; CH_4 series ×. Initial C_2H_4 0·02505 gm. mol/litre; temperature 400° C, time ½ hour.

reaction as is indicated in the diagrams, figs. 5 and 6. We are therefore led to the conclusion that the decomposition of the acetaldehyde is not bimolecular with regard to the aldehyde, but is expressed by,

$$d(C_2H_4O)/dt = K(C_2H_4O)(\phi C_2H_4O + \phi' CH_4 + \phi'' CO).$$

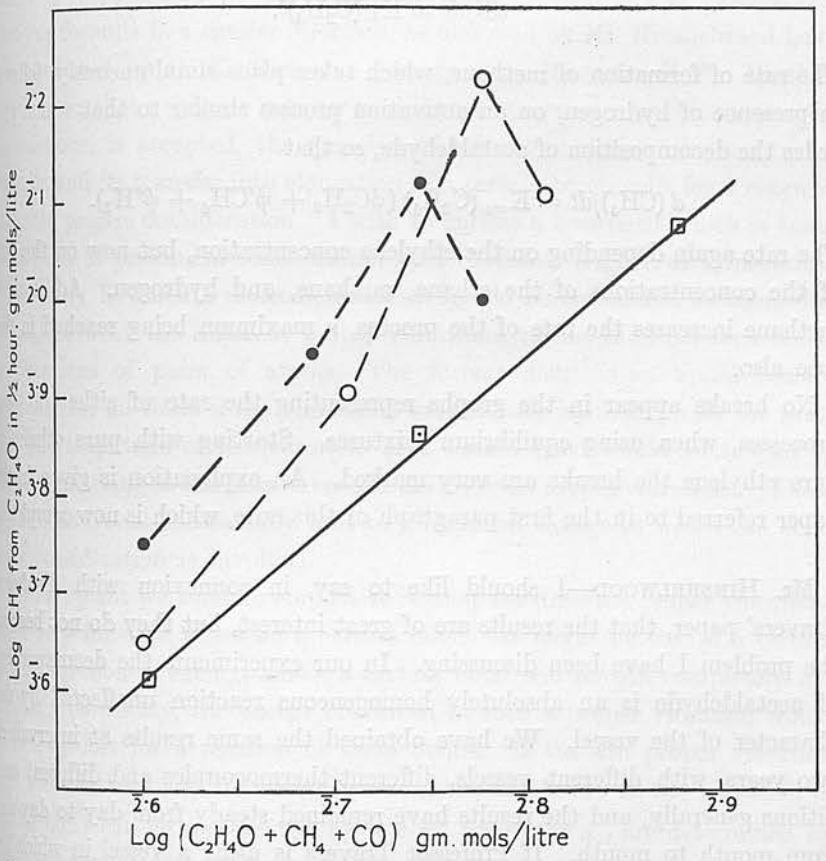


FIG. 6—● CH_4 tube A; ○ CH_4 tube B; □ CO tube B. Initial C_2H_4O 0·03840 gm. mol/litre; temperature 400° C, time ½ hour.

It will now be seen why it is that the initial portions of the graphs representing the rate of decomposition of aldehyde are nearly linear. Also, it is possible to account for the breaks in the graphs without introducing the hypothesis which Mr. Hinshelwood has put forward.

This work was actually undertaken in support of an investigation on the decomposition of ethane and ethylene, and of ethane-ethylene-hydrogen equilibrium mixtures, on which a note was given to the meeting of the Faraday Society at Cambridge in September last. The processes which take place

in the equilibrium mixtures appear to be quite independent of surface conditions, and are therefore most easily studied. The formation of *condensate* appears to be initiated by a *parent* process, the rate of which is measured by the rate of formation of condensate, and which is determined by the ethylene concentration,

$$dR/dt = K_R(C_2H_4)^2.$$

The rate of formation of methane, which takes place simultaneously, follows, in presence of hydrogen, on an activation process similar to that which precedes the decomposition of acetaldehyde, so that

$$d(CH_4)/dt = K_{me}(C_2H_4)(\phi C_2H_6 + \phi' CH_4 + \phi'' H_2).$$

The rate again depending on the ethylene concentration, but now on the sum of the concentrations of the ethane, methane, and hydrogen. Addition of methane increases the rate of the process, a maximum being reached in this case also.

No breaks appear in the graphs representing the rate of either of these processes, when using equilibrium mixtures. Starting with pure ethane or pure ethylene the breaks are very marked. An explanation is given in the paper referred to in the first paragraph of this note, which is now completed.

Mr. Hinshelwood—I should like to say, in connexion with Professor Travers' paper, that the results are of great interest, but they do not bear on the problem I have been discussing. In our experiments the decomposition of acetaldehyde is an absolutely homogeneous reaction unaffected by the character of the vessel. We have obtained the same results at intervals of two years, with different vessels, different thermocouples and different conditions generally, and the results have remained steady from day to day and from month to month. If Professor Travers is using a vessel in which his results vary from day to day owing to drifts, variations of surface activity or other factors, it is interesting, but the difficulty lies in the variation of the catalytic properties of the surface. With regard to the activation energy, our results for the reaction velocity are depicted by the straight line of the Arrhenius equation over a range of 100 degrees. I may also point out that the experiments of Professor Travers are made at an average temperature over 100° lower than ours, where surface effects may well be more prominent; and that with his method of working it must be very difficult to avoid adsorbed oxygen on the silica, which exerts a pronounced, though transient catalytic effect. I think, therefore, that Professor Travers' results, though extremely

interesting, represent a phase of the behaviour of acetaldehyde quite different from the one which I have discussed.

Dr. M. POLANYI—Mr. Hinshelwood's observations and some other data in recent literature show that the dependence of the reaction rate k on pressure p cannot be represented by the simple formula $k = p/(a - bp)$. Deviations from this formula in a similar direction, as observed by Mr. Hinshelwood have been predicted by O. K. Rice and Ramsperger. However, if Mr. Hinshelwood's claim that a definite number of different activated molecules appear in his reactions, is accepted, the question of the accumulation of energy in a molecule and its transfer into elongation of a certain bond, calls for a renewed and more precise consideration. I wish to outline a treatment which is being worked out at present in collaboration with Professor Wigner, of Princeton.

The enegy E which a molecule contains should be considered as being distributed between the different proper vibrations, rather than between bonds or vibrations of pairs of atoms. The former distribution would remain stationary for all times if the vibrations were exactly harmonic. At the same time, the amplitude of the vibration of a certain bond would be subject to fluctuations owing to the interference of the different proper vibrations. These fluctuations would occasionally lead to a chemical change in which the bond under consideration is involved.

The first point we want to emphasize is, that the different proper vibrations are of very different effect on a certain bond. It might be that if a certain proper vibration is excited alone, a certain bond will remain completely unaffected. Obviously, the energy contained in such a proper vibration would be entirely lost for a reaction of these bonds. If the kth proper vibration were alone excited and its energy were ε_k, the amplitude of the vibration of the lth bond can be represented by $\sqrt{\varepsilon_k}\alpha_{kl}$ where the α_{kl} are determined by the mechanical model of the molecule. If all vibrations are excited simultaneously, the elongation of the lth bond is

$$\chi_l = \sum_k \alpha_{kl} \sqrt{\varepsilon_k} \sin \nu_k (t - t_k),$$

where ν_k are the frequencies of the proper vibrations and the t_k are constant phases.

It is evident that these considerations do not affect the theory of reaction rates at high pressure. At low pressures, however, the restriction can be derived that only those states should be considered as activated states, which can lead to the critical elongation without exchange of energy between different

proper vibrations. Activated states with different distributions of energy would have different reaction rates. On these lines it seems easy to account for the presence of different kinds of activated molecules, as required by the experiments of Mr. Hinshelwood.

A further effect should become appreciable at very low pressures. Since the vibrations of no molecule can be considered as strictly harmonic, there will always be some chance for a redistribution of the energy between all the proper vibrations. Thus no molecule will be absolutely stable, which contains in any distribution whatever the energy necessary for the rupture of the critical bond.

Mr. C. Zener—I wish to remark that there are two distinct factors which may greatly reduce the probability that a molecule A should dissociate following collision with a second molecule, the combined energy of the two molecules being sufficient for this dissociation. Firstly the probability may be very small that the critical bond would absorb sufficient energy for dissociation. This may arise either because the molecule A has an extreme reluctance to absorb internal energy (the anomalies in the velocity of sound are familiar examples), or because the energy in A has difficulty in becoming concentrated into the critical bond.

Secondly, even though the bond should have sufficient energy to dissociate, specific perturbations may be necessary for dissociation. This occurs when the symmetries of the electron wave functions associated with the undissociated molecule and with the dissociated molecule in its *lowest* state are different. Some external influence, such as the electric field of a neighbouring ion, will then be necessary to allow a transition between the two states of different symmetry. Professor Lennard-Jones has given an example in which dissociation by a particular bond would require such an external influence. I do not know whether in the complicated molecules which have been studied here such symmetry relations exist; that will require further investigation.

Mr. E. J. Bowen—There is just one feature of the photo-decomposition of gaseous aldehydes and ketones to which Professor Lennard-Jones referred that I should like to develop, and that is their delayed unimolecular decomposition. They all seem to be

$$A + h\nu \rightarrow A^{x} \xrightarrow[(\text{after } 10^{-12} \text{ secs})]{} A' \rightarrow \text{products},$$

similar to the thermal decompositions discussed by Mr. Hinshelwood, except, of course, that the excited levels involved are different. This mechanism agrees with the photo-kinetics; the quantum efficiency is unity or somewhat less, and the reaction rate is independent of the pressure in the gaseous state. There is also strong evidence from work we have been doing with liquid or dissolved substances, such as acetone, glyoxal and diacetyl, which shows that they do not decompose at all unimolecularly in this state, evidently because of the deactivating effect of collisions on the primary excited state A^{x}.

An important question is, of course, how far the nature of the absorption spectra of these substances, which are all diffuse, can be used to throw further light on the mechanism of the decompositions. At one time the mechanism was interpreted as simple predissociation, because the absorption spectra of these substances in the gaseous state begins with fine structure and passes at shorter wave-lengths into diffuse bands. If one asked the question "Does the molecule in fact dissociate?" the old answer was "Yes—no." Now, however, we know that if the delay period is longer than a rotational period the answer may be "Yes—yes," as with formaldehyde.

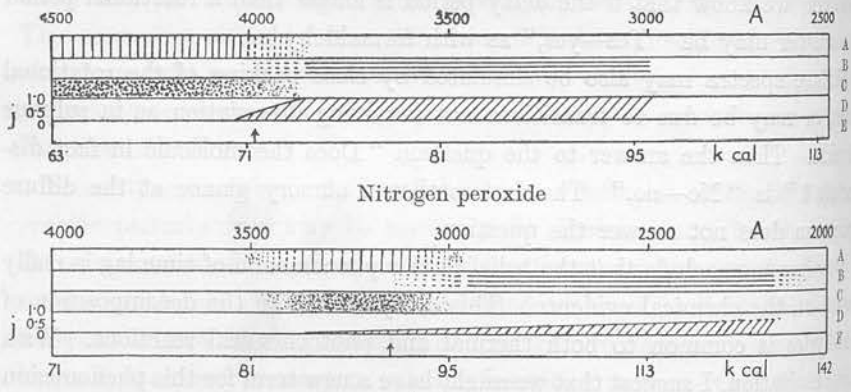
Diffuse spectra may also be simulated by close packing of the rotational lines, or may be due to transitions not involving dissociation as in sulphur dioxide. Then the answer to the question "Does the molecule in fact dissociate?" is "No—no." The fact is that a cursory glance at the diffuse spectrum does not answer the question.

One has to conclude that the belief in this phenomenon of time lag is really based on the chemical evidence. This delay feature in the decomposition of aldehydes is common to both thermal and photochemical reactions. With some hesitation, I suggest that we might have a new term for this phenomenon of delayed unimolecular transitions, the existence of which is really inferred from chemical evidence, because the term "predissociation" has rather vague spectral associations. Possibly the word "menolysis" might prove convenient to describe the phenomenon of unimolecular reaction occurring with a delay between excitation and decomposition, common to both thermal and photochemical reactions.

With regard to the nature of the products of decomposition, it cannot be said that the chemical work is entirely satisfactory. The problem is a very difficult one, because in order to get enough of the products to analyse, one is tempted to take the reaction to completion and also to use a high pressure. It is just under these conditions that these molecules polymerize, and the polymerized product decomposes. Therefore, however carefully the analysis is

made, one does not get the true products of unimolecular decomposition. That is what one finds in comparing other people's results. The question of whether hydrogen is or is not formed in the decomposition of acetaldehyde, for example, is very uncertain. I merely want to focus attention on the accuracy of the present chemical work and to emphasize that any experimental work on these more complex substances must be subject to a very close scrutiny indeed before we can really be satisfied with it.

Dr. R. G. W. Norrish—I should like to touch briefly on the advantages of the photochemical method in studying the energy changes in molecules. First of all, I will illustrate the type of data with which one has to deal. I think it is important in studying any of these reactions to take care to study all the possible aspects of the given reaction. It is necessary to investigate every possible photochemical and spectroscopic aspect: the absorption spectrum, fluorescence, products of decomposition, and also the quantum yield at different wave-lengths.



A Discrete absorption; B Diffuse absorption; C Fluorescence; D Quantum efficiency; E Energy of N-Δ link; F Energy of C-C link

Fig. 7—Nitrogen peroxide acetone

At Cambridge we studied two substances in order to investigate, as far as possible, all these effects together. The first was nitrogen peroxide and the second acetone. (*Slides were shown.*)

In both these substances we have a photochemical threshold of reactivity. This coincides approximately with the onset of diffuseness in the spectrum, and with the cessation of fluorescene. Allowing for a short region of overlap it may be said that fluorescence and fine structure are alternative to diffuseness and reaction. At the photochemical threshold, the energy of the quantum

corresponds fairly closely to the energy of some link in the molecule which is broken. With nitrogen peroxide an oxygen atom splits off; with acetone a free CH_3 radical is eliminated. Now we see how these phenomena are explained; we have the ground state and the upper level; in the upper level it may be possible for an energy switch to occur to an unstable state leading to spontaneous dissociation of the molecule. If this switch occurs within the period of one rotation (10^{-13} sec) we find that the dissociation is evidenced by a diffuse (predissociation) spectrum which has lost its rotational structure. With a polyatomic molecule, however, the energy switch may take place after an interval greater than the period of molecular rotation; the life of a stable excited state is of the order 10^{-8} second, and if during this period the molecule passes through some suitable phase for dissociation, then decomposition may follow even in the region of the spectrum showing fine structure, *e.g.*, as with formaldehyde.

I should therefore like to emphasize that diffuseness is not the best criterion of predissociation. In polyatomic molecules it can be an unreliable guide. The best guide is to be found in the fluorescence. If the fluorescence of a substance is studied at different wave-lengths it is found that the fluorescent limit—the point in the spectrum where fluorescence ceases—is just about coincident with the threshold of photochemical dissociation. Below the threshold the molecule can live again and remit its energy as fluorescence; beyond the threshold it breaks up and fluorescence is no longer possible. That is really a safer criterion of predissociation.

We have studied some other questions relating to aldehydes and ketones. This slide shows that there is essentially a different mechanism in the two cases. When I say "different mechanism" I do not mean that it is very different, but that there are points of difference. If we compare the two substances $\begin{matrix}\mathrm{Me}\\ \mathrm{Et}\end{matrix}\!\!>\!\mathrm{CO}$ and $\begin{matrix}\mathrm{C_3H_7}\\ \mathrm{H}\end{matrix}\!\!>\!\mathrm{CO}$, we find that the former gives us,

$$\tfrac{1}{3}\,(\mathrm{C_2H_6} + \mathrm{C_3H_8} + \mathrm{C_4H_{10}}) + \mathrm{CO}.$$

The ethane, propane and butane are present in roughly equal quantities. We have been able partly to separate those substances by fractional distillation in freezing mixtures and to characterize samples of each by explosion. With isobutaldehyde, however, $\begin{matrix}\mathrm{C_3H_7}\\ \mathrm{H}\end{matrix}\!\!>\!\mathrm{CO}$, which can be compared exactly with the ketone, we have a simpler result. As far as the results of Franck and Pollitzer

go, there are equivalent quantities of CO and propane produced. While the ketone gives a mixture, the aldehyde gives a pure hydrocarbon. This can only be explained by assuming that, instead of coming off as a single molecule as in isobutaldehyde, these two groups in the ketone come off separately. I see no way out of the view that a ketone molecule decomposes either directly into carbon monoxide plus two free radicals (the energy required being 80 kilocalories) or that it breaks up and gives one hydrocarbon radical plus an unstable acyl radical which itself immediately breaks up. It is thus not possible in these experiments to say whether the two radicals come off simultaneously or one after the other, but the chemical effect shows that they must each be liberated separately in the course of the reaction.

The liberation of the radical may be regarded as closely allied to the Auger effect. It is possible to suppose that the carbon atom in the chromophoric group can become excited and then, instead of radiating, can undergo an internal Auger effect which may lead to the rupture of one of its bonds and the decomposition of the molecule.

In contrast to these results, I may mention an interesting result which we obtained when we studied methyl butyl ketone, $CH_3CH_2CH_2CH_2 . CO . CH_3$. This is a ketone with a longer hydrocarbon chain on the one side, and instead of behaving as ketones usually do, to give CO and the hydrocarbons we get nearly quantitatively acetone plus propane—the molecule breaks at a point in the hydrocarbon chain. There is no question about the fact that the quantum is first absorbed by the carbonyl group; the energy for disruption must then be transferred to this bond in the hydrocarbon chain. The question is, how does it get there?

The exact amount of energy involved in this break-down of the hydrocarbon chain is a little difficult to determine. In the analogous reaction of the decomposition of butane, which yields propylene and methane, the energy of activation measured by Pease and Durgan was 65 kilocalories. This measurement does not necessarily give the actual energy which must be applied to that point in the molecule for reaction. It gives an upper limit. The endothermic thermal effect of the reaction is 22 kilocalories, and gives a lower limit. The energy of activation transferred to this point of the molecule must therefore lie between those limits, and in all probability is not less than 30 or 40 kilocalories. That amount of energy has to come out of the original 89 kilocalories which are absorbed by the carbonyl group, and it is more than can be transferred from the excited group to the critical point in the hydrocarbon chain by a pure process of vibration.

We must therefore suggest some other way in which the energy can be degraded. I should like to draw the analogy here, without elaborating it, that we have something akin to an internal collision of the second kind—an "inner sensitization." We are familiar with such processes between two colliding molecules. For example, an excited neon atom may react with a hydrogen molecule to break it into atoms. This only takes place when the excited and unexcited molecules are in close contact, and it is probable that the effect is dependent on resonance between the excited molecule and the primary process; it is not difficult to imagine that the same may also be true here, and that something akin to the radiationless transfer of this kind takes place between the constituent groups of the polyatomic molecule. Further work will be required; we want more data, and these are rather slow to be attained.

Another point to which I should like to draw attention is this: the fluorescent spectrum of acetone has three diffuse bands in the yellow and green. It is difficult at first sight to understand how such diffuse fluorescence can be obtained from a molecule, but provisionally we have come to the conclusion that it may be explained as a type of reversed predissociation; that is to say, that the molecule goes up to a stable upper level and drops back to a lower *unstable* level. This constitutes a new kind of primary process in which a molecule may fluoresce and decompose in one act. By subtracting the emitted quantum from the absorbed quantum, we can calculate the position of this unstable level, and find that it indicates an infra-red absorption between 8000 and 10,000 A. This we have been able to confirm. It seems possible that this unstable infra-red level is identical with that reached thermally in the thermal decomposition of acetone.

The photochemical method of studying the conditions affecting the interchange of energy within large molecules is valuable because by means of the light quantum we can stimulate a given centre in the molecule, and observe what happens to some other part. In using the better known behaviour of diatomic and triatomic molecules as a prototype however, we must not push the analogy too far; it is probable that with new data now accumualting some new types of photochemical decomposition may appear.

Mr. H. W. Thompson—I should like to speak for a few moments on the correlation of certain spectroscopic results with the corresponding photochemical data.

First, however, I would agree with Mr. Bowen about the importance of certain general principles which have hitherto been somewhat obscured,

The first of these is that in polyatomic molecules a diffuse or even continuous absorption spectrum may for a variety of reasons not imply the occurrence of a dissociation process. As Henri has shown* for $COCl_2$ and some other molecules, the three moments of inertia of a Y-shaped molecule containing relatively heavy nuclei are often so great as to produce a very close packing of rotation lines in the bands. This packing can become such that the thickness of the individual lines is greater than their separation, and even under the highest dispersion available a resolution may not be effected. This consideration might *a priori* be expected to apply to the Y-shaped molecule acetone. With formaldehyde, however, the moments of inertia are smaller and rotational fine structure will be detectable. Measurements on fluorescence may, as Dr. Norrish suggests, help to locate the real limit of predissociation but even here the evidence may be misleading if several neighbouring electronic states of the molecule exist.

A second example in which diffuse bands in absorption do not imply a dissociation process is provided by sulphur dioxide. The spectrum consists of two distinct regions, the first stretching from 3800–2500 A and the second, quite different in structure, from 2300–higher frequencies. In the first of these regions there are both sharp and diffuse bands, the diffuseness being developed gradually towards higher frequencies over a considerable range. It is now thought that a predissociation limit is not involved here and that the diffuseness is brought about by a close approach of potential energy curves in the manner discussed by Franck, Sponer and Teller.† I shall refer to this again.

The other general principle which I think it is most important to emphasize is the converse to the above, namely, that the observance of discrete rotational structure does not preclude the possibility of predissociation in the same region. As Mr. Bowen has remarked, this circumstance arises as a result of the greater complexity of polyatomic molecules than diatomic ones. The occurrence of predissociation is determined by whether the vibration of the molecule after initial absorption into such a configuration that a radiationless switch can occur takes place in a time shorter than a natural rotational period. In a polyatomic molecule undergoing a complicated Lissajou motion the time taken to arrive in the switch position may be rather long, giving the molecule time to execute a complete rotation. It is therefore clear that the position of a predissociation limit with a polyatomic molecule will be somewhat ambiguous

* 'Proc. Roy. Soc.,' A, vol. 128, p. 178 (1930).

† 'Z. phys. Chem.,' B, vol. 18, p. 88 (1932).

and often noticeably affected by pressure conditions which may assist or retard the attainment of the switch position.

It seems to me that the case of formaldehyde studied by Dr. Norrish* offers an example of this idea. The quantum efficiency for the photochemical decomposition which, as Dr. Norrish has said, follows the equation

$$H_2CO + h\nu \longrightarrow CO + H_2,$$

is unaffected as the predissociation limit is passed. It is hardly likely that two essentially different mechanisms, the one in the discrete region, involving a primary excitation process, the other in the diffuse region involving primary dissociation, could be compatible with this result; and it is more reasonable to suppose that in the fine structure region predissociation is incipient, the process in both regions being

$$H_2CO + h\nu \longrightarrow H_2 + CO.$$

Mr. Bowen has suggested the term "menolysis" for this delayed dissociation. I had intended to suggest the word "hysterolysis," in accordance with other lag phenomena such as hysteresis.

With regard to specific matters, I would only mention two series of investigations in which these problems, and others mentioned by Mr. Hinshelwood, arise.

The first is in connexion with the photochemical decomposition of molecules containing the chromophoric group SO_2. The absorption spectra of SO_2Cl_2, $(CH_3)_2SO_2$, $(C_2H_5)_2SO_2$ and certain other sulphuryl compounds such as $C_6H_5 . SO_2Cl$ appear to be essentially similar to that of SO_2 itself. As I have already said, this consists of two regions, one of sharp and diffuse bands *ca.* 4000–2500 A, the other beginning at *ca.* 2300 A. SO_2Cl_2 is not photochemically decomposed by ultra-violet frequencies corresponding with the first system of diffuse bands at 3000 A. Photochemical decomposition does, however, occur† with light wave-length 2300 A, and what appears to be a fairly sharp predissociation limit is observed at about this point.

That a case of delayed dissociation is involved here is strikingly shown by the marked dependence of the position of the predissociation limit upon pressure.

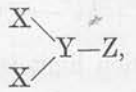
The products of this photodissociation are SO_2 and Cl_2, and the light energy absorbed by the SO_2 group must therefore be transferred, in part at least, to

* 'J. Chem. Soc.,' p. 1518 (1932).

† Andrich, Kangro and Leblanc, 'Z. Electrochem.,' vol. 25, p. 229 (1919); Traum, 'Z. phys. Chem.,' A, vol. 105, p. 356 (1922).

the S-Cl links. The quantum efficiency of the process has not yet been determined, and it is not possible to state with certainty whether both Cl atoms leave the molecule simultaneously or not. The energy quantum absorbed is almost certainly sufficient for this.

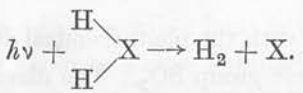
It does seem, to me, important to remember that with many molecules of the type



deformation vibrations of the X-Y links are prominent in the absorption spectra. This will be important in connexion with the photochemical decomposition. With formaldehyde, which decomposes into $H_2 + CO$, the magnitude of the H ⟷ H deformation oscillation is as Herzberg* showed, *ca.* 830 cm^{-1}. With $COCl_2$ that of the Cl ⟷ Cl is *ca.* 582 cm^{-1}; with acetaldehyde that of CH_3 ⟷ H is *ca.* 825 cm^{-1}; and with other molecules it is of the same order.

I am inclined to think that deformation vibrations of this kind may be very important in the decomposition of the molecule.

It is interesting to remember that some time ago Goodeve and Stein† suggested that water, hydrogen sulphide, hydrogen selenide, and hydrogen telluride decompose photochemically, thus



Objections have been raised to this, but it is not definitely disproved.

With $COCl_2$ the absorbed quantum would appear to be quite large enough, taking energy of reorganization into account, for the change $COCl_2 \longrightarrow CO + Cl_2$, and other alternatives such as $COCl_2 \longrightarrow COCl + Cl$ ought to be carefully reconsidered.

I have recently been examining the absorption spectra of a series of compounds in which alkyl radicals are attached to a single atom in the molecule, such as Zn $(CH_3)_2$, Zn $(C_2H_5)_2$, Pb $(C_2H_5)_4$. These spectra often have a surprisingly simple appearance, and although their interpretation is less obvious there seem to be indications that deformation oscillations are prominent.‡ Marked dependence of the Zn $(C_2H_5)_2$ continuum upon pressure suggests that collisions are important in the decomposition.

* 'Trans. Faraday Soc.,' vol. 27, p. 393 (1931).

† 'Trans. Faraday Soc.,' vol. 27, p. 378 (1931).

‡ J. Chem. Soc., 1934, p. 790.

Similar considerations to these appear to apply to the other sulphuryl compounds which I have mentioned. For example, $(C_2H_5)_2SO_2$ is decomposed in the far ultra-violet region into sulphur dioxide and a hydrocarbon residue. As yet the quantum efficiency of this process has not been measured, and the hydrocarbon residue has not been analysed.

With regard to the mechanism of the photochemical decomposition of aldehydes and ketones, I am, as I gather Mr. Bowen is, still a little uncertain of the interpretation of the very extensive and beautiful results described to us by Dr. Norrish. I am of the opinion that these processes involve a primary excitation followed by a dissociation which may be quite considerably delayed. The existence of an excited molecule of relatively long life is in accordance with the fluorescence, the concurrent bimolecular polymerization, and with the very low quantum efficiency resulting from deactivation possibilities. The variation of the quantum efficiency with pressure in the decomposition of acetone, as found by Damon and Daniels,* is also in agreement with the idea of a delayed dissociation.

I find it a little difficult to understand the reason for the essential difference suggested between the mechanism of decomposition for aldehydes and ketones respectively. As Dr. Norrish has shown, all lines of evidence indicate that for aldehydes

$$\begin{matrix} R \\ \\ H \end{matrix}\!\!\diagdown\!\!\diagup CO \longrightarrow RH + CO,$$

but for ketones the intervention of free radicals is suggested:

$$\begin{matrix} R_1 \\ \\ R_2 \end{matrix}\!\!\diagdown\!\!\diagup CO \longrightarrow R_1 + R_2\dot{C}O.$$

The spectral evidence cannot decide between the two possibilities, and it seems to me that analysis of the products with mixed ketones must be the deciding criterion.

I am inclined to agree with Mr. Bowen in regard to the difficulties involved in such analyses. It is surprising, if free methyl radicals are first liberated in the decomposition of $(CH_3)_2CO$, that the reaction proceeds as much as 90% towards ethane formation. I think more than 10% of subsidiary products might have been expected.

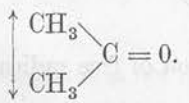
The free radical theory appears to rest mainly on the analyses with methyl ethyl ketone. I have been thinking, quite apart from the points raised by

* 'J. Amer. Chem. Soc.,' vol. 55, p. 2363 (1933).

Mr. Bowen, of the difficulties of obtaining specimens of this substance which are quite free from the diethyl ketone. I believe that the purification is particularly difficult owing to the nature of the vapour pressure curves of mixtures of the different homologues and the close similarity of derivatives which might be used in a process of purification.

It is, moreover, not at all clear how the products with methyl butyl ketone comply with the hypothesis of free radicals.

Dr. Norrish has referred to the question of the real nature of the acetone continuum. Some time ago, using a 1-metre column and pressures down to *ca.* 0·5 mm, I took photographs of this continuum under high dispersion. Above 1 mm the absorption was continuous. At the lowest pressures a peculiarly symmetrical recurring system of diffuse bands was obtained. I believe that Dr. Snow has also obtained some indications of maxima in the continuum, but not quite of the same kind. Dr. Norrish has suggested to me that the effect I observed might have been due to an interference phenomenon caused by a slightly incorrect alignment of the quartz end plates of the absorption tube. There are several reasons why this is improbable, but it may be so. But the inferences to be drawn from the presence or not of such diffuse bands does not affect the view of the decomposition mechanism which I have suggested. The only point would be that the structure of the system might give additional evidence for the presence of deformation oscillations



These may still be involved in the region of bands from 3000–3300 A which have not yet been analysed in detail.

Dr. Norrish—In answer to Mr. Thompson, we were very careful to purify our methyl ethyl ketone by distillation. The origin of the methyl ethyl ketone (from aceto-acetic ester) ensures the purity from anything but traces of other homologous ketones. The purified product boiled constantly to within a tenth or so of a degree of the boiling point given in the International Critical Tables for the barometric pressure of the day.

With reference to the low quantum yield in the decomposition of acetone—that is a point I rather missed when I spoke. According to the results of Damon and Daniels, there is with dry acetone no polymerization and only decomposition, and in that part of the spectrum which is wholly continuous the quantum yield is no greater than 0·4. With these results our own experiments

are in agreement. There is no fluorescence in this part of the spectrum; what therefore happens to those molecules which absorb light and do not decompose? If we have the possibility of an Auger effect in the carbon atom of the excited carbonyl group, leading to the ejection of a CH_3 radical, it is conceivable that only 40% (say) of the molecules will actually decompose, and that this will be conditioned by their internal condition. In a polyatomic molecule such as acetone the several constituent groups are in one sense separate structures with their own rotational and vibrational degrees of freedom. They can thus take from the C-C link some of the energy which would otherwise lead to decomposition, and we get the equivalent of a stabilizing collision. Thus the incipient decomposition is prevented, and we have instead a process of internal degradation to heat. It is possible that external deactivating collisions also play their part.

Mr. C. J. M. Fletcher—Mr. Hinshelwood has given the conclusions which have been drawn from a study of the aldehydes. I should like to describe briefly the experimental results which form the basis of the association of the energy of activation with different parts of the molecule, for the different activated states which exist for the aldehydes. (*Slides were shown.*)

The slide shows, for the same temperature, the variation with pressure of the rates of reaction of formaldehyde, acetaldehyde, and propionicaldehyde. For the last two molecules there are four definite segments, so that four independent modes of decomposition for each molecule may be distinguished. The simplest way to identify the different segments with activation of different parts of the molecule is to compare acetaldehyde on the one hand with formaldehyde, and on the other hand with propionicaldehyde.

The decomposition of formaldehyde is a simple bimolecular reaction up to high pressures. For acetaldehyde also, the curve indicates that there is a reaction which remains bimolecular up to the highest pressures used. The rate of reaction of formaldehyde is satisfactorily explained by the simplest type of activation, *i.e.*, of two square terms. At high pressures the same is also true of acetaldehyde. It seems, therefore, that there is a bimolecular decomposition of acetaldehyde, similar to that of formaldehyde, in which the energy of activation goes directly to that part of the molecule, whose activation is responsible for carbon monoxide being split off.

The segment at the lowest pressures measured, may be identified by a comparison of the curves for acetaldehyde and propionicaldehyde. As the slope of the line is greatest for this segment, the rate at which activated molecules are

produced is greatest for the associated reaction; however, the energy of activation is considerably larger than at higher pressures. These two facts taken together, mean that the energy of activation is contained in many square terms. As this segment is relatively more important in propionicaldehyde than in acetaldehyde, it may be reasonably assumed that activation is concerned with that part of the molecule which is different in the two substances—*i.e.*, with the alkyl group. This hypothesis accounts for the large number of square terms concerned, and also for the fact that as the alkyl group is remote from that part of the molecule which is responsible for decomposition, the probability of decomposition is small, so that the curve becomes horizontal at low pressures. The theory is further confirmed by an entirely different experimental fact. The primary products of decomposition of propionicaldehyde at normal pressures are mainly carbon monoxide and ethane; but at lower pressures, hydrogen and ethylene appear in increasing proportions; the extent to which they increase, agrees closely with the extent to which the lowest segment becomes more prominent. The reaction predominating at low pressures must therefore involve activation of the alkyl group, to account for the production of hydrogen and ethylene as primary products in the decomposition of propionicaldehyde.

It is not possible to associate the two intermediate segments with activation of any particular vibrations of the acetaldehyde molecule, but they may be connected with activation of the carbonyl group, or other vibrations concerned with the carbon atom of the —CHO group.

Professor E. K. Rideal, F.R.S.—Since the time is very late I will shorten my communication to a few remarks.

Ever since Professor Lindemann put forward suggestions for the mechanism of a unimolecular reaction, about thirty have been investigated. They have all involved the inference of a number of squared terms (S). We may note that as the internal energy has to surge into a particular link before deactivation by a secondary collision occurs we are interested not only in the problem whether the necessary amount of energy is actually present in the molecule, but also if this energy be present how long it takes to migrate to the reactive bond. This problem in its turn involves the investigation of the influence of the molecular structure, *i.e.*, the path by which the energy is conveyed both on the probability of energy transfer and on the time required for such transfer.

In respect to the first point, viz., the amount of internal energy actually possessed by the molecules at the reacting temperatures I confess that I am

somewhat sceptical as to the realities of the magnitudes deduced by the application of the collision theory of activation. We may note that 25 squared terms are required for cyclopropane, 38 for tertiary butyl alcohol, 25 for azomethane and 28 for ethyl azide. I cannot help suspecting that some of these reactions will turn out to involve chains, especially when we recollect that over the usual range of reacting temperature only one CH linkage in seven can contain a quantum of vibrational energy equal to *ca.* 2kT, and the main contribution to the internal energy must come from the heavy atoms in the molecule. More work on the specific heats of these substances is evidently desirable.

The next consideration is, if the energy be really there, what are the relationships between the structure and the conditions of transmission of this energy. In the first place how far can E and S be correlated with constitutional factors.* The ethers (6–12 S terms) and the azo compounds (25–40 S terms) are the only homologous series studied hitherto and the former show no well-defined regularities. The increase in S effected by substitution of $-O-$ for $-N=N-$ would appear to be surprisingly large. The azo decompositions that have been investigated, and the work is being extended to other compounds of this type by Dr. Gwyn Williams in my laboratory, do show a fairly regular change of E and S with increasing molecular complexity, as shown in the following table, all computed with $\sigma = 3\text{–}6\ 10^{-8}$ cm.

Structure	Temparature range °C	E Energy of activation cals./gm. mol.	S No. of square terms
$CH_3{-}N=N{-}CH_3$	270 — 330	51,200	25
$CH_3{-}N=N{-}C(CH_3)_2H$	250 — 330	47,430	33
$(CH_3)_2CH{-}N=N{-}CH(CH_3)_2$	250 — 290	40,900	>40
$C_6H_5CH=N{-}N=CHC_6H_5$	318 — 353	57,000	>32
$C_6H_5CH_2{-}N=N{-}CH_2C_6H_5$	Gaseous decomposition at 200°		

We may note that whilst E changes relatively slightly the number of squared terms rises rapidly with the increase in molecular complexity ; also from a study of organic reactions in solution we may conclude that constitutional influences are operative over a considerable distance in the molecule, although damping in a carbon chain usually occurs after the fourth carbon atom. It is, of course, also well known that the relative chain lengths in chain reactions are subject

* The value of S may be affected by a steric factor, and by incomplete redistribution of energy in molecular collisions.

to large variations and a comparison of chain lengths in well-established chain decompositions with molecular complexity would appear important.

Another method of approach to the problem of energy transfer is to ensure that the reacting group is maintained constant, attach to it another group, which can grow in a homologous series, and examine the effect of chain length on E and S. This problem is at present under examination by Dr. Melville, who has commenced a study of a simple polymeric reaction. The scanty evidence derived from technical sources suggests to us that frequently in building up a polymer we are not dealing with a bi-molecular reaction between first of all simple molecules followed by a sequence of bimolecular reactions between bi- and tri-merides (and so on) respectively, but that simple molecules add themselves progressively to growing chains and that as the chain gets longer the facility of addition increases but not indefinitely. If this view be correct the properties of the growing polymer must surely be a continuous function of its size and thus certain generalized equations may be used to describe the behaviour and so yield some information about the mechanism of the growth, the number of squared terms involved, the target area and the energy transfers involved.

Naturally conditions are most favourable in the gas phase at low pressures. The results of a preliminary investigation on the polymerization of acetylene by light from a mercury vapour lamp in the presence of mercury vapour lead to some interesting conclusions.

Without going into experimental details the facts (at pressures from 0·01 to 10 mm) are (*a*) that the reaction consists in association of an excited mercury atom with an acetylene molecule, this complex then participating in a series of collisions with normal acetylene molecules thus building up a polymer, the photochemical chain length at room temperature being about 10, and rising gradually to about 100 at 250° C., and subsequently decreasing to about 50 at 500° C (*b*). The chain length is independent of pressure, of intensity of light, and does not appear to depend on whether the tube is packed or not. It may be added that there is evidence for a secondary polymerization of the products of the photo reaction on the walls of the reaction vessel.

The reaction kinetics are thus reasonably simple and permit, therefore, a quantitative enquiry into the details of the process. The experiments lead to the conclusion that termination of the chains, *i.e.*, a cessation of increase in size of the polymer, occurs by the collision of a chain carrier (polymer) with an acetylene molecule and not by the collision of two (polymer) carriers nor by the spontaneous decomposition of the carrier. Similarly, however, the

propagation reaction involves the collision between the chain carrier and an acetylene molecule. The absolute value of the length of the chain, *i.e.*, the polymer size, and its variation with temperature will therefore be determined simply by the nature of the energy transformations involved when an acetylene molecule hits a polymer molecule. The first problem is thus to evaluate the ratio and if possible the absolute value of the velocity coefficients for the propagation and termination reactions.

Two extreme situations may be imagined. (*a*) There are two separate kinds of collision involving different energies of activation, numbers of square terms and steric factors. (*b*) There is only one type of collision and the subsequent emergence of a chain carrier from the collision is determined by the probability of the distribution of energy in the collision complex itself, which may vary with temperature.

Suppose k_1, k_2, k_3, ..., and k'_1, k'_2, k'_3, ..., denote respectively the velocity coefficients for propagation and for termination then it can be shown, by setting down the equations expressing the stationary concentrations of each individual polymer molecule, that the chain length is given by the equation

$$\nu = 1 + \left\{1 + \frac{k_1}{k_1 + k'_1} + \frac{k_1}{k_1 + k'_1} \times \frac{k_2}{k_2 + k'_2} + \cdots \frac{k_1}{k_1 + k'_1} \cdots \frac{k_{n-1}}{k_{n-1} + k'_{n-1}}\right\}.$$

If, for simplicity, it is assumed that $k'_1/k_1 = k'_2/k_2 = x$ then

$$\nu = 1 + \left\{ + \frac{1}{1+x} + \frac{1}{(1+x)^2} + \frac{1}{(1+x)^3} \cdots \right\}.$$

If x is not too small the series converges rapidly and therefore summing to ∞ terms

$$\nu = 2 + 1/x,$$

when the chains are long

$$\nu = 1/x = k_1/k'_1 = \frac{\alpha e^{-E/RT}}{\alpha' e^{-E'/RT}} = \alpha/\alpha' \, e^{-(E-E')/RT},$$

where α and α' are coefficients containing (*a*) the factors to increase the rate of activation when the number of square terms exceeds two, and (*b*) steric factors. The chain length increases with temperature and hence $E - E'$ must be positive, and is actually at 25° C, 4000 cal. The quantity $e^{-(E-E')/RT}$ is therefore much less than unity, but since ν is 10 at 25°, α/α' is very much greater than unity and is equal at 25° C to 3×10^4.

This calculation rules out the possibility that the propagation or termination of the growth of the polymer is determined by an energy distribution in a given

collision. The next problem is to separate steric and square term factors. Progress is now less certain, but considering the steric factors first, it is probably true to say that only a comparatively small portion of the growing polymer molecule has the property of adding on an acetylene molecule, while termination might occur by partial disintegration of the polymer by an impact of an acetylene molecule at any part of the polymer, and thus there should be a large steric factor for propagation whereas in fact the reverse state of affairs exists since $\alpha \gg \alpha'$.

On account of the chain length reaching a maximum, *i.e.*, $d\nu/dt = 0$, then

$$\frac{d\ln \alpha/\alpha'}{dT} = -(E - E')/RT^2,$$

and therefore α/α' must be a function of the temperature. Hence it is the variation in this quantity which has the effect of counterbalancing and finally more than counterbalancing the increase in chain length brought about by the factor $e^{-(E-E')/RT}$.

Including square terms and steric factors (F and F')

$$\frac{\alpha}{\alpha'} = \frac{F}{F'} \frac{(E/R)^{(S/2-1)}}{(E'/R)^{(S'/2-1)}} T^{\frac{1}{2}(S'-S)} \frac{(S'/2-1)!}{(S/2-1)!}$$

whence

$$\frac{d\ln \alpha/\alpha'}{dT} = \frac{\frac{1}{2}(S' - S)}{T}$$

$$\tfrac{1}{2}(S - S') = (E - E')/RT \quad \text{or} \quad S - S' = 8.$$

Thus at 250° C eight more square terms participate in propagation than in termination.

Until the absolute value of E or E' is determined the absolute value of S, S' and F and F' cannot be determined.

Preliminary experiments using a method which need not be described here indicate that E is of the order 5000 cal.

It is interesting to note that under these conditions, ethylene does not polymerize in a manner similar to acetylene, and no increase in the velocity of polymerization occurs when the temperature is raised from 15° C to 300° C.

Mr. Ubbelohde—The point of Mr. Hinshelwood's observations has been that in thermal activation there is no evidence that there is anything but an increasing number of vibrations of the molecule in the ground level. Furthermore, the observation of Richards and Reid* likewise only dealt with the ground

* 'Nature,' vol. 130, p. 739 (1932)

level. The curious thing that has been observed there is that not every collision between molecules leads to the transfer of vibrational energy; only one in 10^5 may be effective. Nevertheless, certain impurities, such as hydrogen, are far more efficient in promoting this exchange of the translation of vibration than ethylene itself. Consequently, from the point of view of reaction mechanism, when we find catalysts such as Mr. Hinshelwood has found—hydrogen in the decomposition of aldehydes and ethers and iodine in the decomposition of ethers—it is interesting to enquire whether the physical investigation bears out the simple interpretation that the effect of these catalysts is simply to favour the transmission of vibrational energy in the ground state.

I just want to make one remark about the sort of physical tests we use at the moment to check the chemical equations. The chief method is the change in velocity of sound with frequency. If the impurity which is found to have the catalytic effect promotes exchange of vibrational energy it will, of course, shift the region of dispersion. Another physical check comes from thermo-conductivity. In the same way, if the impurity affects the sound transmission it likewise raises the thermo-conductivity of the gas abnormally.

Another point is that we know from the qualitative theory of the transmission of vibration to molecules that unless the molecules penetrate fairly deeply into one another's fields, transmission will not take place. Consequently, if hydrogen is more effective in exciting vibrations of ethylene than ethylene itself, we expect to find other physical evidence for such a penetration. In the ethers there is indeed evidence that iodine in the vapour state has some very loose combination with ether, with a heat of formation of 3k. cals., this indicates penetration by molecules to an abnormal extent, compared with the ordinary Van der Waals' attraction.

Mr. Hinshelwood, in reply—The points raised have been so varied and interesting, and some of them so much beyond my power to deal with, that to summarize would be rather difficult. We have seen what an extraordinary variety of phenomena come within the scope of this discussion. On the question that Mr. Ubbelohde has just asked, I suggested to Dr. Fromherz, of Munich, who worked in my laboratory last summer, that substances which form addition compounds with acetaldehyde at low temperatures might catalyse its decomposition at high temperatures, but experiments which he made gave negative results in this respect.

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THE KINETICS OF THE REACTION BETWEEN HYDROGEN AND NITROUS OXIDE

PART II

III—EFFECT OF OXYGEN

By

H. W. Melville

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The Kinetics of the Reaction between Hydrogen and Nitrous Oxide Part II

By H. W. MELVILLE, Senior Student, Exhibition of 1851

(Communicated by J. Kendall, F.R.S.—Received May 8, 1934)

An analysis of the mechanism of the thermal hydrogen-nitrous oxide reaction in silica vessels by the kinetic method has shown that it is a chain process.* The experiments were confined to a comparatively narrow pressure range and the evidence for chain propagation, although quite definite, required confirmation. The present paper is therefore concerned with the kinetics under a much wider variety of conditions. First, the experiments have been extended to pressures below 30 mm; second, photochemical methods have been employed to shed more light on the individual steps of the reaction and to demonstrate unequivocally its chain character; third, in view of the close similarity of the hydrogen-nitrous oxide and hydrogen-oxygen reactions, a detailed study has been made of the effect of small amounts of oxygen on the former reaction. The results of these experiments all lend additional strong support to the chain hypothesis.

Small alterations to the apparatus were made. A glass spring gauge was employed for measuring low pressures. One end of the furnace was provided with a quartz lens in order to focus the light from the mercury lamp on the reaction bulb; the cathode of the lamp was water cooled. Arrangements were also made for inserting a hollow silica cell between the lamp and the lens so that filters could be used for controlling the intensity and wave-length of the light reaching the bulb. Direct photo dissociation of the nitrous oxide molecule was not attempted since (*a*) absorption of photochemically active light at low pressures in small bulbs is not complete, (*b*) the intensity of the lines of the mercury arc in the absorption region of nitrous oxide is weak. Recourse was therefore made to mercury sensitization in spite of a little additional complication.

Low Pressure Dark Reaction

Several questions arise when the reaction is carried out at somewhat lower pressures. The high pressure experiments indicated the importance of gas

* Melville, 'Proc. Roy. Soc.,' A, vol. 142, p. 524 (1933).

phase termination with but a small proportion of wall inhibition. At low pressures, it would be anticipated that the mechanism would involve wall processes to a much greater extent. In the thermal decomposition of nitrous oxide, it has been shown that the collisions leading to activation below 50 mm are different from those above this pressure, for example, the energy of activation increases from 50 to 58 k. cal. (Musgrave and Hinshelwood put the upper limit at 64 k. cal.) It was thus of importance to find if there was, in consequence, any fundamental alteration in the kinetics of the hydrogen-nitrous oxide reaction. Further, the chain length at high pressures increases with decreasing pressure and there is therefore a chance that the reaction might become explosive, if the pressure were reduced sufficiently, in the sense that an upper explosion limit had been passed.

The lower limit to the pressure range was fixed at about 2 mm. It was undesirable with this type of apparatus to go below this pressure, for several complicating factors intrude. The withdrawal of water vapour by the phosphorus pentoxide gives rise virtually to a small water vapour diffusion pump which would make the manometer readings unreliable. Similarly, the effect of thermal effusion would be difficult to calculate in the transition region where the mean free path of the molecules begins to become comparable with the dimensions of the connecting tubes.

The total order of the reaction was determined by finding the effect of pressure on (*a*) the initial rate (R), and (*b*) the time required ($t_{\frac{1}{2}}$) for the reaction to go half-way to completion. If there is concordance in these two methods, nitrogen cannot exert any appreciable influence on the course of the reaction. The data are given in Table I.

In fig. 1, $\log_{10}$ R and $\log_{10} t_{\frac{1}{2}}$ have been plotted against $\log_{10} p$, but the lines obtained are not quite straight; the slope tending to decrease at high pressures. For the $\log_{10}$ R–$\log_{10} p$ curve, the mean slope is $1 \cdot 8$ and hence the order of the reaction, as measured by the influence of p on R, is very nearly two. The slope of the $\log_{10} t_{\frac{1}{2}}$–$\log_{10} p$ curve is $-0 \cdot 7$ and again, therefore, the order is almost two. The decrease in the order at higher pressures is in accordance with the results in Part I, where the total order has fallen to unity.

The effect of nitrogen, and probably that of argon too, should thus be negligible in view of the correspondence in the values obtained for the orders. A few experiments are quoted in Table II, in which nitrogen or argon was present initially, and inspection of the values of Δp show these to be practically independent of the pressure of inert gas.

Table I

Temperature 750° C, 5 cm tube, 1 : 1 mixture

Initial pressure	27·0	18·38	12·98
Time	Δp	Δp	Δp
mins			
0	0·0	0·0	0·0
0·5	1·4	0·80	0·56
1·0	3·4	2·02	1·18
1·5	5·2	3·06	1·93
2	6·4	3·96	2·41
3	8·2	4·96	3·13
4	9·3	5·74	3·66
6	10·5	6·58	4·30
8	11·1	7·18	4·68
10	—	7·50	4·96

p is in mm of mercury.

Initial pressure	6·52	3·20	1·60
Time	Δp	Δp	Δp
mins			
0	—	—	—
0·5	0·12	0·03	—
1	0·40	0·10	—
2	0·76	0·42	—
3	1·05	—	—
4	1·30	0·58	0·20
6	1·66	0·67	0·27
8	1·85	—	—
10	2·06	0·96	0·35

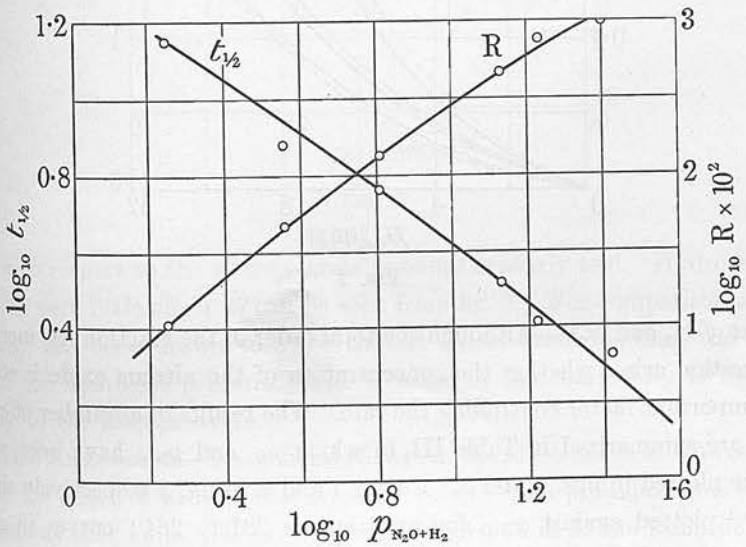

FIG. 1

Table II

750° C, 1 : 1 mixture

$p_{H_2+N_2O}$	9·63	9·92	9·57	9·75	$p_{H_2+N_2O}$	9·89	9·59	9·94
p_A	—	4·80	9·61	14·40	p_{N_2}	—	4·61	9·60
t	Δp	Δp	Δp	Δp		Δp	Δp	Δp
2	1·93	1·74	1·58	1·25		2·15	1·82	1·76
3	2·30	2·40	2·20	2·10		2·56	2·40	2·54
4	2·70	2·84	—	2·70		2·91	2·80	2·94
5	—	—	2·96	—		—	—	—
6	3·20	3·32	—	3·35		3·46	3·32	3·45
8	3·55	3·60	—	3·55		3·76	3·64	3·74

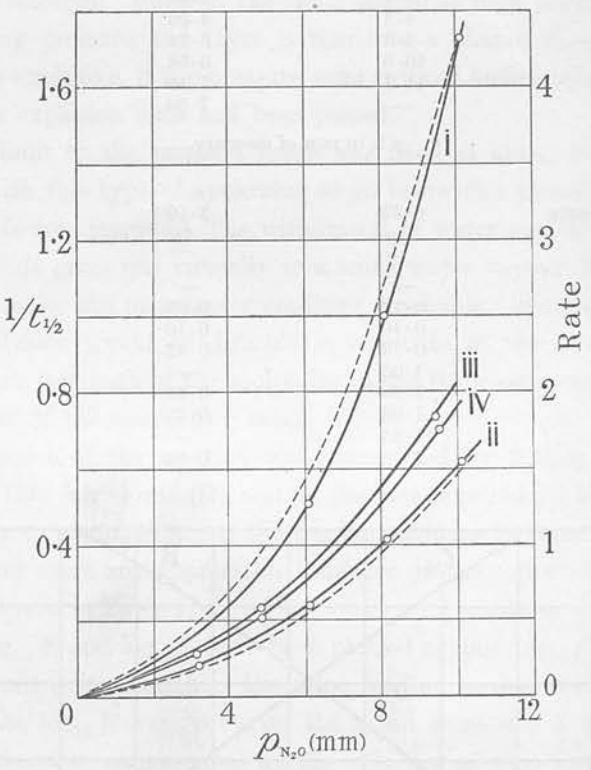

FIG. 2

Effect of H_2 *and* N_2O—Although the total order of the reaction has increased, the question arises whether the concentration of the nitrous oxide is still the most important factor controlling the rate. The results of a number of experiments are summarized in Table III, in which p_{H_2} and p_{N_2O} have been varied, and are plotted in figs. 2 and 3. Curves i and ii in fig. 2 respectively show R and $t_{\frac{1}{2}}^{-1}$ plotted against p_{N_2O} for experiments 281 to 284; curves iii and iv refer to experiments 362–364. The dotted lines are drawn assuming that the rate is proportional to the square of p_{N_2O}. These results demonstrate that the

Table III

Experiments 281–284, 725° C. Experiments 358–364, 750° C.

Experiment No.	p_{H_2}	p_{N_2O}	R	$t_{\frac{1}{2}}$	$t_{\frac{1}{2}}^{-1}$
282	2·02	3·23	0·20	9·0	0·111
283	1·98	6·07	0·60	1·95	0·51
281	2·02	8·11	1·04	1·00	1·00
358	4·77	4·91	0·64	4·10	0·244
359	9·61	4·81	0·79	3·36	0·297
360	16·22	4·93	0·96	2·86	0·35
361	24·40	4·95	0·96	2·86	0·35
362	4·83	4·85	0·58	5·0	0·20
363	4·80	9·58	1·85	1·42	0·70
364	4·86	15·10	2·50	1·00	1·00

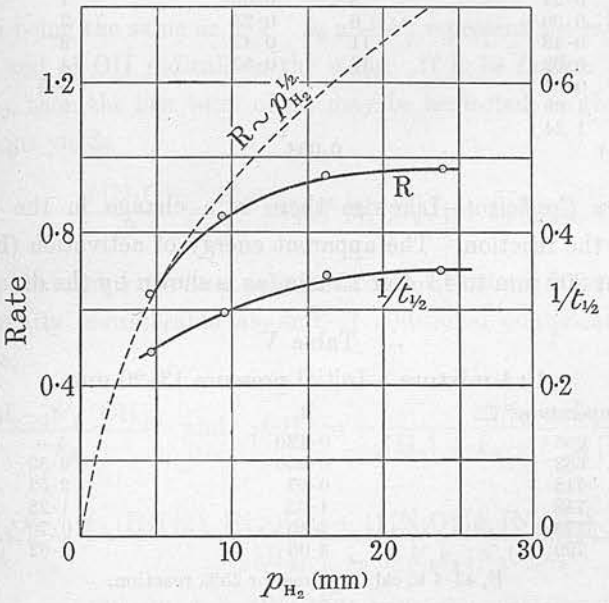

FIG. 3

order with respect to the nitrous oxide pressure is nearly two. Hydrogen has, however, very little effect as can be seen from fig. 3. For comparison a curve $R \sim p_{H_2}^{\frac{1}{2}}$ has been drawn to show that R varies even less than the square root of the hydrogen pressure. The increase in the total order is thus due entirely to the nitrous oxide.

Packing Experiments—The general change in the kinetics has also its counterpart in the effect of packing the reaction vessel. The procedure was exactly the same as that employed in experiments 243–247 in I, the same bulb and packing material being employed. Effectively the diameter is decreased from 2·5 to 0·7 cm. That wall inhibition has increased is fully borne out by the

results in Table IV, where the rate decreases six times compared with a two-fold decrease at 100 mm. If the chains were terminated solely on the walls, the decrease should be $(2 \cdot 5/0 \cdot 7)^2$ or 13 times. Even at 5 mm there must therefore be a small amount of gas phase termination.

Table IV

Temperature 768° C. 1 : 1 mixture

Empty		Packed		Empty	
Initial pressure	4·94		4·92		4·71
t	Δp	t	Δp	t	Δp
0	—	0	—	0	—
0·5	0·07	1	0·03	0·5	0·08
1	0·24	3	0·06	1	0·17
1·5	0·36	6	0·23	2	0·34
2	0·48	11	0·43	3	0·47
3	0·62	16	0·55	4	0·59
4	0·84			6·5	0·86
6	1·09			9	1·03
8	1·24				
R	0·24		0·034		0·17 mm/min

Temperature Coefficient—Likewise there is a change in the temperature coefficient of the reaction. The apparent energy of activation (E) rises from 30·5 k. cal. at 200 mm to 43·4 at 13 mm, as is shown by the data in Table V.

Table V

1 : 1 mixture. Initial pressure 13·20 mm

Temperature ° C	R	$t_{\frac{1}{4}}$
655	0·120	—
683	0·250	6·50
718	0·67	2·52
749	1·33	1·28
778	2·45	0·70
799	3·05	0·62

E, 43·4 k. cal. $t_{\frac{1}{4}}$ time for 25% reaction.

These calculations of E are not quite exact, for constant pressures instead of concentrations were used. The corrected values are, however, easily obtained for the kinetics of the reactions are known; at high pressure E is 36·5 k. cal. and at low, E is 49·5 k. cal.

Explosions—As with the high pressure reaction, explosions could be obtained if the temperature was raised sufficiently. There were no signs of any sharp limiting pressures, either upper or lower.

Mechanism of the Reaction

In further elaborating the scheme of reactions put forward in I, the following observations have to be accounted for, the increase in the total order, in

packing effect and in the apparent energy of activation. It will be supposed that the mechanism of initiation and propagation remain unaltered, but the strong inhibition by walls shows definitely that most of the chains are terminated there. To simplify the equations, gas phase termination will be neglected. The equations expressing the stationary concentrations of H and of OH will therefore be :

$$\frac{d[\mathrm{H}]}{dt} = \mathrm{I} + k_5[\mathrm{OH}][\mathrm{H_2}] - k_4[\mathrm{H}][\mathrm{N_2O}] - k_9[\mathrm{H}] = 0, \quad (1)$$

$$\frac{d[\mathrm{OH}]}{dt} = \mathrm{I} + k_4[\mathrm{H}][\mathrm{N_2O}] - k_5[\mathrm{OH}][\mathrm{H_2}] - k'_9[\mathrm{OH}] = 0, \quad (2)$$

the notation being the same as in I. k_9 and k'_9 represent the rate of diffusion of H atoms and of OH radicals to the walls. If it be further assumed that $k_5[\mathrm{H_2}] \gg k'_9$, then the last term of (2) may be neglected, so that solution of these equations yields

$$-\frac{d[\mathrm{N_2O}]}{dt} = \frac{2k_4}{k_9}[\mathrm{N_2O}]^2\{k_1[\mathrm{N_2O}] + k_2[\mathrm{H_2}]\}, \quad (3)$$

if, as before, the chains are long. Reinstatement of the last term in (2) leads to an apparently considerable amount of additional complication. In this circumstance,

$$[\mathrm{H}] = \frac{2\mathrm{I} - k'_9[\mathrm{OH}]}{k_9} \quad \text{and} \quad [\mathrm{OH}] = \frac{2\mathrm{I}/k_9 + \mathrm{I}}{k_5[\mathrm{H_2}] + k_9 + k'_9k_4[\mathrm{N_2O}]/k_9},$$

whence

$$-\frac{d[\mathrm{N_2O}]}{dt} = \frac{k_5[\mathrm{H_2}]\{2k_4[\mathrm{N_2O}]/k_9 + 1\}[\mathrm{N_2O}]\{k_1[\mathrm{N_2O}] + k_2[\mathrm{H_2}]\}}{k_5[\mathrm{H_2}] + k_9 + k'_9k_4[\mathrm{N_2O}]/k_9}. \quad (4)$$

An examination of (4) will show that if $k'_9 = 0$, this equation reduces to (3). First of all, (4) can be much simplified on account of a previous valid assumption, namely, that the chains are long, *i.e.*, k_9 can be neglected compared with $k_4[\mathrm{N_2O}]$ and $k_5[\mathrm{H}]$. k'_9/k_9 can be approximately calculated from the diffusion theory, and for a 1 : 1 mixture is equal to 0·25. (4) reduces to

$$\frac{d[\mathrm{N_2O}]}{dt} = \frac{2k_5[\mathrm{H_2}]k_4[\mathrm{N_2O}]^2\{k_1[\mathrm{N_2O}] + k_2[\mathrm{H_2}]\}}{k_9\{k_4[\mathrm{N_2O}]/4 + k_5[\mathrm{H_2}]\}}. \quad (5)$$

At high pressures, the theoretical equation agreeing best with the results was based on the assumption that $k_5 \gg k_4$. In (5), this inequality is still further increased by taking into account the different rates of diffusion of H and OH. On making this further simplification, (5) reduces to (3). Again it may be

pointed out that the experimentally observed order is rather less than the theoretical value. At low pressures, k_9 should be inversely proportional to the total pressure which would accentuate the difference between theory and experiment. The absence of acceleration of the reaction by argon and nitrogen, however, indicates that there may be sufficient gas phase termination to render k_9 effectively constant in the pressure range employed. (5) also shows that the increase in order is due to N_2O, which is in agreement with experiment. It is surprising to find that p_{H_2} does not affect R as much as (5) would allow. This might be due to a surface effect, in that adsorption of hydrogen on the wall may increase with pressure causing a concomitant increase in the efficiency of chain-breaking collisions.

The temperature coefficient of a chain reaction may be interpreted most simply by considering the reaction to consist of three separate parts : initiation (I), propagation (P), termination (T), each having its own temperature coefficient. At high and at low pressures, the kinetic equations may be generalized as follows :—

$$R = \frac{P \cdot I'}{T'} \exp\{(E_{T'} - E_P - E_{I'})/RT\} = \frac{P \cdot I'}{T'} \exp(-E'_R/RT), \qquad \text{(low pressure)}$$

$$R = P \cdot (I''/T'')^{\frac{1}{2}} \exp\{(E_{T''/2} - E_{I''/2} - E_P)/RT\} = P \cdot (I''/T'')^{\frac{1}{2}} \exp(-E''_R/RT), \qquad \text{(high pressure)}$$

where T′ and T″ refer to the low and high pressure reactions and E'_R and E''_R to the apparent energies of activation. Termination at high pressures is mainly due to ternary collisions, a reaction which, so far as is known, has practically no energy of activation, $E_{T''} = 0$ and since $-E''_R = E_{T''/2} - E_{I''/2} - E_P$, $E_P = 7{\cdot}5$ k. cal., assuming $E_{I''} = 58$ k. cal. E_P represents the energy of activation of the reaction $H + N_2O = OH + N_2$. This value is perhaps somewhat low if the following calculation is made. It will be shown later that, at 10 mm and 700° C, the chain length is of the order 10^2. A hydrogen atom, under these conditions, if generated in the middle of the bulb, would make about 10^6 collisions before reaching the wall. If it is further assumed that on every collision with the wall, the atom is adsorbed and rendered incapable of further chain propagation, then it must make $10^6/2 \times 10^2$ or 5×10^3 collisions with N_2O before reaction occurs. This corresponds to a value of E_P of 17 k. cal., and is of course a minimum, for if the collisions with the walls are partly elastic, E_P will be correspondingly increased.

Substituting $E_P = 7{\cdot}5$ k. cal. in (6) and putting $E_{I'}$ 50 k. cal. $E_{T'} = 8$ k. cal. It may be remarked that $E_{T'}$ agrees moderately well with the values for the wall termination process in the H_2–O_2 reaction obtained by Grant and Hinshelwood* for silica surfaces (12·8 k. cal.), and by Frost and Alyea† for a KC coated Pyrex surface (13·5 k. cal.), which are also based on the assumption that termination in a ternary collision requires no activation.

Whatever may be the true significance of $E_{T'}$, there is no doubt about its sign, which shows that the efficiency of wall removal of the carriers increases with the temperature. A similar behaviour might be expected in analogous reactions, for example, the combination of organic radicals. In practice, however, methyl and ethyl radicals are *less* easily destroyed as the temperature of the surface is raised,‡ that is, the sign of E_T is different. It must be pointed out that in the latter experiments, the results were obtained directly, whereas in the H_2–N_2O and H_2–O_2 reactions, $E_{T'}$ is calculated indirectly on assumptions which may not be exact.

As at high pressures, the rate of the H_2–N_2O reaction is considerably faster than the decomposition of N_2O. For example, at 650°, the rate of water formation was 1·21 mm per minute at 22·52 mm (1 : 1 mixture). In the same 5 cm tube, N_2O decomposed at 0·14 mm per minute at 740°, the initial pressure being 12·58 mm. At 650° and 11 mm, the rate would be 0·017. The ratio is 95 and will not alter much with pressure since the orders of the two reactions are equal. Similarly, temperature will have little effect on the ratio.

Effect of NO_2—The primary object of studying the effect of this molecule was to determine whether it might induce the explosive combination of H_2 and N_2O at temperatures where the normal rate is small. No such phenomenon was observed, although the NO_2 slightly accelerated the rate. Another point of dissimilarity thus exists between the present reaction and those chain oxidations in which the addition of NO_2 leads to explosive combination at lower temperatures.§

Photochemical Experiments

A number of problems have arisen in the discussion of the low and high pressure reactions which may be solved by employing photochemical methods.

* 'Proc. Roy. Soc.,' A, vol. 141, p. 29 (1933).

† 'J. Amer. Chem. Soc.,' vol. 55, p. 3227 (1933).

‡ 'Trans. Faraday Soc.,' vol. 30, p. 186 (1934).

§ H_2–O_2, Gibson and Hinshelwood, 'Trans. Faraday Soc.,' vol. 24, p. 559 (1928); Thompson and Hinshelwood, 'Proc. Roy. Soc.,' A, vol. 124, p. 219 (1929); Norrish and Griffiths, *ibid.*, vol. 139, p. 147 (1933). CO–O_2, Semenoff and others, 'Z. phys. Chem..' B, vol. 6, p. 307 (1930).

By this means, the initiation of chains can be independently controlled so that the propagation and termination factors may be observed operating together. The first important point was to demonstrate that a photochemically produced hydrogen atom could induce the reaction of several molecules of N_2O, and thus show without doubt that the reaction is of the chain type. Further, it was also necessary to find if the chain length calculated from the thermal experiments agreed with that obtained photochemically, in order to support the hypothesis about initiation by oxygen atoms. Experiments on the effect of intensity of the radiation should provide confirmation of the mechanism of the termination of the chains. Having obtained this information, the next problem to be elucidated is the form of the propagation factor and how it is influenced by H_2, N_2O and by temperature.

It will be shown later that small amounts of oxygen exert a very marked accelerating influence on the H_2–N_2O reaction, and the question arises whether this effect is due to a change in the initiation or the propagation factor; both may be affected.

In obtaining the photochemical chain length, the measurements were made from room temperature up to temperatures where the thermal becomes comparable with the photochemical reaction. The pressures were so chosen that a constant concentration of gas was present in the reaction vessel; the data are given in Table VI. For comparison, a run with a 1 : 1 H_2–O_2 mixture at room temperature was carried out.

The results in Table VI are further tabulated in Table VII. The net photochemical rate in Table VII is the observed rate of reaction with the light on minus the rate of the thermal reaction. It will be observed that in experiments 757 and 759, the rates of the H_2–N_2O and H_2–O_2 reaction are nearly the same. In Table VII, it has been assumed for the purposes of calculation that the quantum yield of the former reaction at 25° C is unity. It may be greater than this, but would certainly not exceed two. The photochemical chain length is then simply calculated by finding the ratio of the rates at the higher temperature and at 25° C. The assumption made is that the quenching of the mercury resonance radiation is not appreciably influenced by temperature; this is supported, at any rate for hydrogen, by the measurements of Cario and Franck.*

The photochemical chain length at 650°, (116) is somewhat greater than the ratio of the rates of the H_2–N_2O reaction, and the decomposition of N_2O. The

* 'Z. Physik,' vol. 37, p. 619 (1926).

Table VI

1 : 1 mixture. 5 cm tube

757 25° C		759 23° C		766 294° C		767 400° C	
t	*p*	*t*	*p*	*t*	*p*	*t*	*p*
0	9·65	0	0·56	0	15·15	0	16·67
5	9·59	10	9·39	2	15·03	2	16·27
10	9·49	21	9·21	5	14·72	4	15·78
20	9·36	30	9·08	10·5	14·34	6	15·35
30	9·20	40	8·95	15	13·98	8	14·98
40	9·09	52	8·87	21	13·55	10	14·55
50	8·90		(H_2–O_2)	25	13·22	15	13·75
R	0·015		0·017		0·082		0·234

768 502° C		763 558° C		765 603° C		764 603° C (thermal)	
t	*p*	*t*	*p*	*t*	*p*	*t*	*p*
0	18·67	0	19·13	0	19·13	0	20·18
1	17·94	0·5	18·37	0·5	18·05	1	19·88
2	17·06	1	17·60	1	16·75	2	19·59
3	16·32	1·5	16·70	1·5	15·68	4	19·22
4	15·68	2	16·00	2	14·83	6	18·88
6	14·33	3	14·70	2·5	14·07	8	18·55
8	13·41	4	13·50	3	13·42	10	18·27
10	12·47	6	12·00	4	12·50	12	17·94
		8	11·13	5	11·93		
R	0·76		1·70		2·60		0·265

770 650° C (photo)		771 650° C (thermal)		773 740° C (thermal)		772 740° C Decom. of N_2O	
t	*p*	*t*	*p*	*t*	*p*	*t*	*p*
0	22·40	0	22·50	0	25·54	0	12·58
0·25	21·10	0·5	21·86	0·25	23·82	5	12·93
0·50	19·90	1	21·40	0·50	22·78	10·5	13·35
0·75	19·04	1·5	20·84	1	18·23	15	13·60
1	18·24	2	20·48	1·5	17·27	20	13·83
1·5	17·02	3	19·84	2	16·70	25	14·10
2	16·02	4	19·28	3	15·83	30	14·39
2·5	15·33	6	18·48				
3	14·72	8	17·60				
5	13·43						
R	5·25		1·21		8·9		0·140

Table VII

Temp. °C	Photo. rate	Thermal rate	Net photo. rate	Photo. chain length (ν)	$\log_{10}\nu$	$10^3/T$
25	$1·55 \times 10^{-3}$	—	$1·55 \times 10^{-3}$	1	0·00	3·36
294	$5·43 \times 10^{-3}$	—	$5·43 \times 10^{-3}$	3·5	0·544	2·203
400	$1·40 \times 10^{-2}$	—	$1·40 \times 10^{-2}$	9·0	0·954	2·141
502	$4·07 \times 10^{-2}$	—	$4·07 \times 10^{-2}$	26·2	1·418	1·764
558	$8·90 \times 10^{-2}$	—	$8·90 \times 10^{-2}$	57·3	1·76	1·485
603	$1·36 \times 10^{-1}$	$1·31 \times 10^{-2}$	$1·23 \times 10^{-1}$	79·0	1·90	1·790
650	$2·34 \times 10^{-1}$	$5·4 \times 10^{-2}$	$1·80 \times 10^{-1}$	116·0	2·06	1·154
740	—	$3·5 \times 10^{-1}$	—	—	—	1·088

The rates of the reactions are expressed as R/p.

discrepancy is increased if, as has been assumed, one oxygen atom from the nitrous molecule initiates two chains, but the numbers are of the same order of magnitude. The conclusions which may therefore be drawn are (*a*) that chains can be propagated in H_2–N_2O mixtures, (*b*) that nearly every oxygen atom derived from the thermal dissociation of an N_2O molecule leads to the initiation of two chains. In these calculations no account has been taken, in the thermal reaction, of the possibility of hydrogen molecules activating N_2O by collision; this would have the effect of decreasing the thermal chain length. It may be that when such a collision takes place, H_2O is formed immediately after, so the collision is unfruitful so far as chain starting is concerned. The close proximity of N_2 would facilitate the formation of H_2O by removing a considerable amount of the energy which would normally cause H_2O to dissociate.

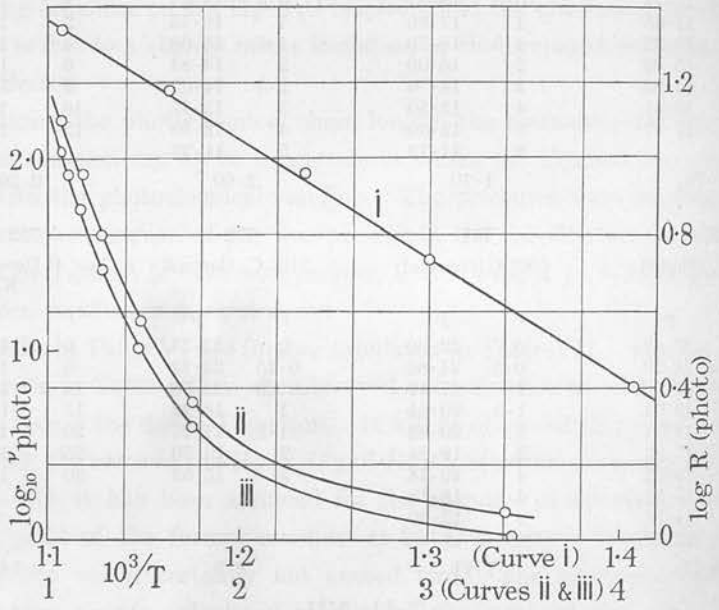

FIG. 4—Curve ii is displaced upwards for clarity.

It is also improbable that $\nu_{ther.} < \nu_{photo}$, on account of the O atom reacting with N_2O to yield NO, since Harteck* found that reaction of O with H_2 is very much faster than with N_2O. Another anomaly is that ν_{photo} increases with, but $\nu_{ther.}$ is independent of, temperature.

The results in Table VII and other data are illustrated in fig. 4 in which log ν_{photo} is plotted against 1/T. The slope of the curve is not constant but

* 'Z. phys. Chem.,' B, vol. 12, p. 327 (1931).

increases from 25° to 400°, thereafter remaining constant. A similar variation in the slope of $\log R - 1/T$ curves is also obtained in the mercury photosensitized H_2–O_2 reaction, which Taylor and Salley* ascribe to branching. The curvature is, however, most pronounced at high temperatures. It is very doubtful whether such an explanation would hold in the present instance. What is more reasonable to suppose is that there is a change in the mechanism of the reaction as the temperature is raised from 25° to 400° C; for instance in deducing the kinetic equation, the assumption was made that the chains were long: Table VII shows this is no longer valid. Curve i in fig. 4 has been plotted with a larger 1/T scale in order to demonstrate more clearly that there is no curvature between 440° and 630° C; the energy of activation is 13·8 k. cal., which may be compared with zero for the thermal reaction. At high pressures on the other hand, the apparent energy of activation (36·5 k. cal.) is lower than that of the initiation process (58), and consequently the chain length must decrease with temperature. The origin of this phenomenon is due primarily to self-neutralization of the chains in the gas, as may be seen from the following equations,

$$R_{H_2-N_2O} = P\left(\frac{I''}{T''}\right)^{\frac{1}{2}} \exp\{(-E_P - E''_I/2 + E''_T/2)/RT\},$$

$$R_{N_2O} = I'' \exp(-E''_I/RT).$$

But

$$\nu_{ther.} = \frac{2R_{H_2-N_2O}}{R_{N_2O}} = \frac{P}{(I''T'')^{\frac{1}{2}}} \exp\{(-E_P + E''_I/2)/RT\},$$

since $E''_T = 0$.

In order that $d\nu/dT$ be negative, $E''_I/2$ must be greater than E_P.

Effect of N_2O *and of* H_2—In Table VIII, the effect of total pressure on the rate is given and in Table IX, the effect of hydrogen. The thermal reaction was negligible at 533° C. It will be observed that the initial rate of reaction increases with pressure, but the values of T/2 (T/2 time for 50% reaction) also increase with pressure and hence the order must lie between zero and unity. If the values of Δp in Table IX be compared for different hydrogen pressures, it will be seen that a five-fold variation has hardly any influence. Nitrous oxide must then be responsible for the increase in rate of Table VIII.

The initiation term in the kinetic equation will now be $\frac{[H_2]}{[H_2]+[N_2O]}$, assuming to a first approximation that (*a*) atomic hydrogen starts the reaction

* 'J. Amer. Chem. Soc.,' vol. 55, p. 96 (1933).

(*b*) N_2O merely deactivates Hg', (*c*) the quenching radii of the two molecules is the same. Let $I = \frac{K[H_2]}{[H_2]+[N_2O]}$, K is a constant and is proportional to mercury vapour pressure and to the intensity of the light. On substituting this value of I in equations (1) and (2) and performing the simplifications in deriving (5),

$$-\frac{d[N_2O]}{dt} = \frac{k_4}{k_9}[N_2O] \cdot \frac{K[H_2]}{[H_2]+[N_2O]}.$$

Table VIII

5 cm tube, 1 : 1 mixture, 533° C

$p_{H_2+N_2O}$	6·73	10·04	13·44	16·80	22·40
t	Δp	Δp	Δp	Δp	Δp
0·5	0·33	0·33	0·38	0·48	0·50
1	0·58	0·69	0·66	0·82	0·90
2	1·00	1·14	1·28	1·46	1·65
4	1·61	1·97	2·18	2·58	2·80
6	1·99	2·54	2·90	3·40	3·90
8	2·28	2·96	3·54	4·04	4·80
10	2·50	3·34	4·11	4·86	5·78
15	2·82	3·96	4·90	6·00	7·08
T/2 (min)	4·3	5·8	7·4	8·4	9·7

Table IX

p_{N_2O}	4·81	4·80	4·77	4·86	4·77
p_{H_2}	9·57	14·40	19·23	23·98	4·80
t	Δp	Δp	Δp	Δp	Δp
0·5	0·36	0·31	0·32	0·36	0·27
1	0·82	0·63	0·66	0·70	0·62
2	1·48	1·30	1·32	1·34	1·44
3	1·94	1·95	1·88	2·00	1·63
4	2·48	2·42	2·30	2·48	2·21
6	—	3·17	3·10	3·14	2·83
8	—	3·67	3·58	—	3·39
10	—	—	—	—	3·87

The small effect of hydrogen would seem to indicate that I is independent of $[H_2]$ and hence there is evidence of quenching by H_2 being more efficient than that by N_2O. I would then become equal to K. The important point is that, compared with the thermal reaction, the order with respect to $[N_2O]$ has fallen sufficiently to show that N_2O is not only responsible for initiation in the thermal reaction, but that the propagation factor is very nearly proportional, to $[N_2O]$. The general features of the thermal reaction are thus supported by photochemical data.

Effect of Argon—Argon does not deactivate Hg' very efficiently so that I should be unaffected by its presence ; any effect would therefore be due to its influence on propagation or termination. None was found, using 10 mm of A

and 10 mm of a 1 : 1 mixture. Again, there is agreement between the photo and thermal data.

Effect of Intensity—It has been shown in deducing (6) that at low pressures, the rate of reaction should be proportional to the intensity. At high pressures, the equation for the photochemical reaction will be

$$-\frac{d[N_2O]}{dt} = k_4[N_2O]\left(\frac{K[H_2]}{[H_2]+[N_2O]} \cdot \frac{1}{k_8\{[N_2O]+[H_2]\}}\right)^{\frac{1}{2}},$$

and therefore the rate ought to be proportional to the square root of the intensity.

Preliminary experiments were carried out with a sector wheel containing two apertures, the angle of which could be varied. If the mean life of the chains is greater than the time between successive exposures, then, effectively, variation in this angle will alter the (mean) intensity of the light admitted to the reaction vessel.* If, however, the chains are of very short duration, alteration of the sector opening will merely change the time of exposure and thus will not provide the information on the intensity law which is being sought. In the latter circumstance, the data may show whether or no there is an induction period or a reaction after the light has been cut off.

The results of two experiments are illustrated in fig. 5, the upper curve referring to the low pressure reaction (16 mm of 1 : 1 mixture) at 570°, the lower curve was obtained at a pressure of 100·5 mm and 510° C. The wheel was rotated at about 120 r.p.m., R is the initial rate of reaction. The points at 180° show the value of the rate without the rotating sector. It will be observed, first of all, that the lines are straight and pass through the 180° points. This alone would indicate that there is no appreciable dark reaction after the light is cut off, for if there were, the 180° points would lie below the prolongation of the R–ϕ lines. These lines, however, do not pass through the origin and hence there would appear to be some dark reaction. In varying the time of illumination by altering the angle of the aperture, the interval between exposures is likewise changed, owing to the method of construction of the discs. That this time of darkness does not account for any significant part of the variation of R with ϕ is shown by the data in Table X. The rate of rotation of the sector was reduced so that the interval of darkness was increased from 0·12 to 5 seconds, but the values of Δp are nearly identical and hence the after-effect must be complete in less than 0·12 second.

* *Cf.* Griffith and McKeown, "Photo Processes," p. 664.

Table X

Sector angle 90°, pressure 16 mm, temperature 570° C, 1 : 1 mixture

Speed	t	0·5	0·75	1·0	1·5	2	2·5	3
3 r.p.m.	Δp	0·54	0·75	1·20	1·56	2·06	2·46	2·86
120 ,, ...	Δp	0·53	—	1·05	1·63	2·13	2·57	2·96

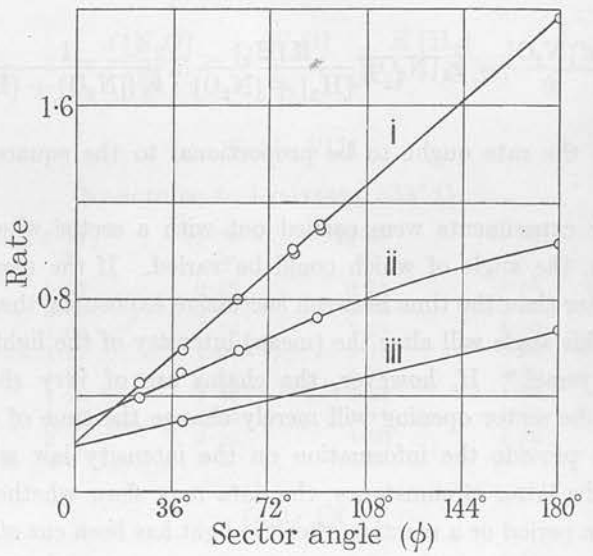

FIG. 5—(i) Low pressure, 570° C; (ii) high pressure, 510° C; (iii) high pressure, 470° C.

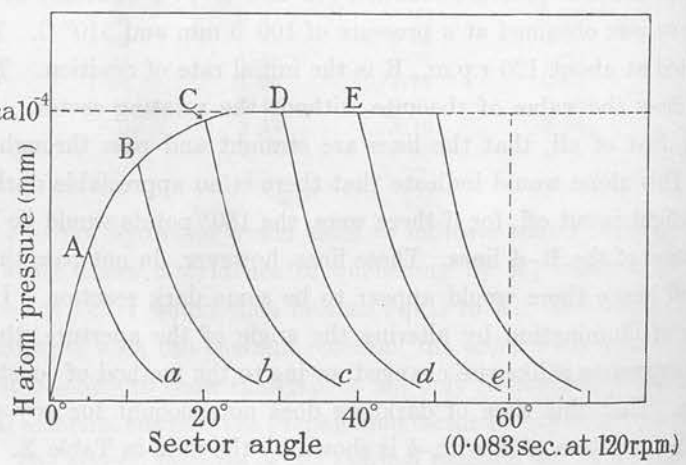

FIG. 6

The course of the reaction during the time of exposure and the interval before the next period of illumination occurs may be illustrated by fig. 6, which is only approximately drawn to scale, the H atom concentration being

plotted against the sector angle or time of illumination for a given velocity of rotation. The reaction velocity is assumed to be so small that the stationary concentration of atomic hydrogen does not alter appreciably owing to the decrease in $[H_2]$ and $[N_2O]$. When the light is first switched on at O, [H] rises, attains a certain steady value and then falls at E when illumination ceases. The lines Aa, Bb, .., show how [H] falls when the light is cut off at A, B, C, etc. The number of H_2O molecules formed in time t is proportional to $\int_0^t [H]\,dt$ and for a sector opening corresponding to E, will be proportional to the area OAEe. The rate of decrease of [H] will depend on the method of termination of the chains. At low pressures, $-d[H]/dt = k_9[H]$, whereas at high pressures, $-d[H]/dt = k'_6[H]^2$.

Consider the low pressure reaction first, then the equation giving the value of [H] at any time during illumination is

$$\frac{d[H]}{dt} = I - k_9[H],$$

or

$$[H] = I/k_9\,(1 - e^{-k_9 t}).$$

During the ensuing dark period,

$$-\frac{d[H]}{dt} = k_9[H],$$

or

$$[H] = [H]_T\, e^{-k_9 t},$$

where $[H]_T$ is the value [H] attains before the light is cut off after time T. The rate R is proportional to the number of H_2O molecules produced for a given time of experiment. If the proportionality factor be K then

$$R = K\int_0^T [H]_L\,dt + K\int_0^{T_0-T} [H]_D\,dt,$$

where L and D refer to the reaction in the light and in the dark. T_0 is the time required for the disc to rotate 180°. Substituting from the above equations

$$R/K = I/k_9\int_0^T (1 - e^{-k_9 t})\,dt + \int_0^{T_0-T} I/k_9\,(1 - e^{-k_9 T})\,e^{-k_9 t}\,dt,$$

or

$$R/K = \frac{I}{k_9}T - \frac{I}{k_9^2}(1 - e^{-k_9 t})\,e^{-k_9(T_0-T)}.$$

When k_9^{-1} is small compared with T, the second term may be neglected, and therefore

$$R/K = I \,.\, T/k_9.$$

The R–ϕ curves should be straight and pass through the origin. It will also be observed from the above equation that if $T = 0$, then $R = 0$.

The results at high pressures may be treated in a similar way. During illumination

$$1/k'_6 \,.\, \frac{d\,[H]}{dt} = I/k'_6 - [H]^2,$$

or

$$[H] = (I/k'_6)^{\frac{1}{2}} \tanh \sqrt{Ik'_6}\, t,$$

where $k'_6\,[H]^2$ is the rate at which H atoms are removed in ternary collisions. In the dark

$$-\frac{d\,[H]}{dt} = k'_6\,[H]^2$$

or

$$[H] = \{k'_6\, t + 1/[H]_T\}^{-1},$$

whence

$$R/K = \int_0^T [H]_L\, dt + \int_0^{T_0 - T} [H]_D\, dt$$

$$= \int_0^T (I/k'_6)^{\frac{1}{2}} \tanh \sqrt{Ik'_6}\, dt + \int_0^{T_0 - T} (k'_6\, t + 1/[H]_T)^{-1}\, dt$$

$$= 1/k'_6 \,.\, \log \cosh \sqrt{Ik'_6}\, T + 1/k'_6 \log \left\{ \frac{T_0 - T + 1/k'_6\, I \,.\, \coth \sqrt{Ik'_6}\, T}{1/k'_6\, I \,.\, \coth \sqrt{Ik'_6}\, T} \right\}.$$

If $T = 0$, $R/K = 0$. When T is large so that $e^{(Ik'_6)^{\frac{1}{2}}T} > e^{-(Ik'_6)^{\frac{1}{2}}T}$, then

$$R/K = 1/k'_6 \left\{ (Ik'_6)^{\frac{1}{2}} T + \log \frac{(Ik'_6)^{\frac{1}{2}} T + 1}{2} \right\}.$$

When $(Ik'_6)^{\frac{1}{2}}\, T > 1$, the second term in the above equation will be relatively unimportant compared with the first and again therefore, a straight line passing through the origin is to be expected, the slope of which should be proportional to the square root of the intensity of the light from the lamp. The cause of the positive intercept on the rate axis is not revealed by this analysis. In the course of the photochemical experiments, it was observed that after the light was cut off, the reaction still continued but at a much reduced speed. It was somewhat difficult to obtain accurate measurements, but the effect lasted some 30 seconds, and hence would not be revealed by the variation in section speed employed in Table X. Moreover, the dark reaction could not be due to the

gradual decrease in the concentration of hydrogen atoms for these diffuse to the wall in a time very much less than 30 seconds (*cf.* p. 744). It may happen that although the H atoms are removed by the walls very rapidly, they do not immediately recombine and so may be capable of starting new chains from the surface long after the light has been cut off. Virtually, then, a dark reaction is superposed on the photo reaction, but its existence depends primarily on the previous illumination of the gas. The magnitude of the rate is not, however, sufficiently great to cause the R–ϕ curves (at high pressure) to follow the relation $R \sim \phi^{\frac{1}{2}}$. Since the 180° point lies on the same line as the other points, the dark reaction will become of greater importance as the sector angle decreases; the relation will be a linear one for the interval between successive periods of illumination is small compared with half-life of the dark reaction. The intercept (0·2 mm/min) therefore represents the velocity of the dark reaction. Direct measurements of the after-effect showed that the rate was about 0·2 at 16 mm and 570° C; for instance, in one experiment in which the light was switched on and off at 1 minute intervals, the dark reaction amounted to 0·20, 0·13 and 0·10 mm after 25%, 50% and 60% reaction respectively.

Similar photochemical after-effects have been observed* in the ammonia sensitized H_2–O_2 reaction where some reactive atom or radical is deposited on the walls after explosion and is capable of exploding a fresh mixture without requiring illumination. The after-effect for the mercury photosensitized stable reaction was also observed in the present experiments, but the results were not very reproducible. It may be mentioned in this connection that a lag between the adsorption and subsequent re-evaporation of chain carriers has formed a successful postulate† in explaining some of the features of the induction period in certain chain reactions, such as hydrocarbon oxidations.

According to the calculations made on p. 744, the life of a reaction chain or hydrogen atom is at least 10^{-2} seconds, if it reaches the wall. Even at higher pressures, the mean life of the hydrogen atom is probably of the same order of magnitude since there is still wall-inhibition. This calculation gives a minimum value for the energy of activation of $H + N_2O$. The sector experiments yield a maximum value. Had the mean life of the hydrogen atom been greater than 10^{-1} second, then the $R - \phi$ at high pressures should have exhibited a well-defined curvature. As the line is straight, the mean life is

* Farkas, Haber and Harteck, 'Z. Electrochem.,' vol. 36, p. 711 (1930).

† Semenoff, 'Z. phys. Chem.,' B, vol. 11, p. 464 (1931); 'Phys. Z. Sowjet,' vol. 1, p. 546 (1932); 'Trans. Faraday Soc.,' vol. 28, p. 878 (1932).

less than 10^{-1} seconds, which corresponds to an energy of activation of 21·5 k. cal.

So far as these experiments go, they cannot provide the information on the rate intensity relationship which is being sought. Recourse was therefore made to wire screens, but these were not satisfactory; finally a liquid filter consisting of a solution of carbon tetrachloride in specially pure *n*-hexane was employed.*

The data at high and at low pressures are given in Table XI.

Table XI

Pressure 16·0 mm, temperature 568° C

Intensity.....	1·00	0·91	0·80	0·68	0·51
t	Δp	Δp	Δp	Δp	Δp
0·5	0·53	0·52	0·35	0·30	0·24
1·0	1·07	0·95	0·86	0·66	0·52
1·5	1·57	1·36	1·22	0·95	0·66
2	2·01	1·79	1·59	1·27	0·95
3	2·77	2·48	2·17	1·85	1·32
4	3·27	2·95	2·65	2·26	1·71
5	3·84	3·47	3·18	2·70	2·06

Pressure 100·0 mm, temperature 510° C

Intensity.....	1·00	0·68	0·51	0·38
t	Δp	Δp	Δp	Δp
2	1·5	1·2	0·9	0·7
4	3·4	2·6	2·2	1·6
6	4·9	4·0	3·2	2·3
8	6·5	5·0	4·2	3·0
10	7·9	6·2	5·0	3·6
15	11·1	8·4	—	4·8

The results in Table XI and some others are plotted in fig. 7. The full line represents $R \sim I$, and the dotted curve $R \sim I^{\frac{1}{2}}$. It will be observed that the low pressure results lie close to the line, whereas the high pressure experiments lie nearer the curve; therefore the termination reaction involves the participation of one carrier at low pressure and two at high pressure. The $R \sim I^{\frac{1}{2}}$ law could not be expected to hold exactly at 100 mm for it was shown in Part I that there is still a considerable amount of termination on the walls. The important point, however, is that these measurements support the hypothesis already put forward to explain the way in which the chains are stopped.

Discussion

It remains now to mention a few points not specifically dealt with in the discussion of the data. The interpretation of the present results does not

* Melville and Walls, 'Trans. Faraday Soc.,' vol. 29, p. 1255 (1933).

alter the scheme of reactions set forth in Part I. The equivalence of the thermal and photochemical chain lengths shows that a hydrogen or an oxygen atom can set off a similar reaction cycle, but unfortunately, the calculations are not sufficiently exact to demonstrate whether hydrogen molecules can activate nitrous oxide molecules by collision. It would also seem most probable, at low pressures, that the combination of H atoms is responsible for termination. Schemes involving OH radicals do not give kinetic equations in agreement with the facts. The intensity measurements quite definitely show that only one carrier is concerned, and in conjunction with the packing experiments there is no doubt that a wall reaction is responsible for termination.

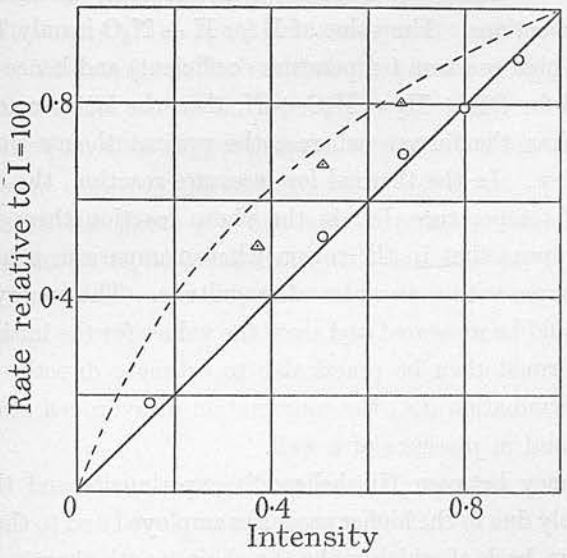

FIG. 7

Since Part I was written, new data* have become available on the effect of various gases in promoting the combination of hydrogen atoms. Argon is about as effective as the hydrogen molecule. Now in the high pressure experiments, argon does not inhibit the reaction (for a 1 : 1 mixture) and hence neither can H_2; N_2O must therefore be more efficient than H_2 as a third body. This greater effective collision diameter may possibly be due to the chemical reaction,

$$H + H + N_2O = H_2O + N_2,$$

rather than to the physical removal of energy,

$$H + H + N_2O = H_2 + N_2O.$$

* L. Farkas, private communication.

But N_2O cannot be very much more efficient than H_2, for the rate of reaction becomes independent of $[H_2]$ when this is large. Such a result implies that an inhibition term containing $[H_2]$ appears in the denominator of the kinetic equation.

In all the reactions studied, the effect of hydrogen is, in general, small, the nitrous oxide concentration mainly controlling the rate. This is consistent with the theory that the propagation and initiation factors (in the thermal reactions) contain $[N_2O]$. In outline, then, the experimental facts are in agreement with the theory, except that the total order is usually a little lower than that expected theoretically. There are, nevertheless, some inconsistencies in the scheme, concerning in particular the values of the energies of activation of the several reactions. The value of E for $H + N_2O$ is only 7 k. cal. (calculated from the high pressure temperature coefficient) and hence if the value of 15 be accepted for $OH + H_2 = H_2O + H$, then the latter reaction would be much slower than the former, whereas the present theory would incline to the opposite view. In the thermal low pressure reaction, the chain length is independent of temperature, but in the photo reaction there is an increase, although it happens that in the region where comparison can be made, the chain lengths agree within an order of magnitude. The energy of activation of $H + N_2O$ could be measured and since the values for the initiation processes are known, it would then be practicable to estimate directly the energy of activation of termination (*i.e.*, the combination of hydrogen atoms) in a three body collision and in presence of a wall.

The discrepancy between Hinshelwood's experiments and those described above is probably due to the higher pressures employed and to the accumulation of water vapour, both of which make the chain length short. It is, however, difficult to understand how Dixon and Higgins succeeded in obtaining spontaneous inflammation at comparatively low temperatures. The composition of the gas in a flow system could, of course, vary within wide limits, but it is hardly possible for this to give a velocity sufficiently great to inflame the gases.

The author desires to thank the Royal Commissioners for the Exhibition of 1851 for a Senior Studentship and the Trustees of the Moray Research Fund of Edinburgh University for a grant.

Summary

The kinetics of the hydrogen-nitrous oxide reaction have been studied in the pressure region 1–30 mm and at temperatures from 500° to 750° C. Under

these conditions, the rate of reaction is proportional to the square of the nitrous oxide concentration, is nearly independent of that of the hydrogen, is markedly retarded by packing the vessel, but is not affected by nitrogen or argon. The energy of activation is 49 k. cal. The kinetics are different from those of the high pressure reaction studied previously, but practically complete correlation may be obtained by postulating that the chains now end by the combination of H atoms on the walls.

Chains may also be started by H atoms produced by optically excited mercury atoms. The photochemical chain length agrees with that of the thermal reaction, the latter being based on the measured rate of dissociation of N_2O. At low pressures, the photo reaction rate is proportional to the N_2O concentration, to the intensity of the light, but is independent of the concentration of H_2, N_2 and A. The energy of activation is 17 k. cal. At high pressures, the rate varies as the square root of the intensity, which shows that the chains end by self-neutralization, thus supporting the theory given for the thermal high pressure reaction.

Experiments on the photo reaction with a rotating sector are described. The results are shown to be consistent with the remainder of the data.

The Kinetics of the Reaction between Hydrogen and Nitrous Oxide
III—*Effect of Oxygen*

By H. W. Melville (Senior Student, Exhibition of 1851)

(Communicated by J. Kendall, F.R.S.—Received May 8, 1934)

One of the most striking dissimilarities between the hydrogen-oxygen and hydrogen-nitrous oxide reactions is the absence in the latter of sharp explosion limits, a feature characteristic of the former. Another important difference is that propagation of chains in the H_2-N_2O mixtures is rather less easy than in H_2-O_2, for the photochemical chain length is smaller for H_2-N_2O than for H_2-O_2 at the same temperatures and pressures (see below). It has, however, been postulated that the carriers in the two reactions are identical and that at least one step, viz.,

$$OH + H_2 \rightarrow H_2O + H,$$

is common to both reactions. The differences in the propagation factors would therefore be due to these reactions

$$H + N_2O = OH + N_2$$

and

$$H + H_2 + O_2 = OH + H_2O,$$

or

$$H + O_2 = HO_2$$

$$HO_2 + H_2 = OH + H_2O.$$

It may be anticipated that termination processes will be somewhat similar, and consequently the observed differences in the thermal reactions will also be partly due to initiation reactions.

In this paper, an attempt has been made to study the two reactions under similar conditions so that propagation and initiation reactions may be separated from each other. Experiments have therefore been made on the effect of small quantities of oxygen on the high and low pressure thermal reactions and on the high and low pressure photo reactions. As will be shown below, oxygen exerts a very marked effect in increasing the rate. Its addition has been controlled so that the increase is comparable with the rate of reaction of the oxygen-free mixtures, in order that the stationary concentration of the chain carriers and the nature of the termination reactions should be similar for the two reactions.

To account for the sharp explosion limits in H_2-O_2 mixtures, branching is supposed to occur in one of the reaction cycles, and the reaction presumed to be responsible for this is

$$H + H_2 + O_2 = 2OH + H,$$

or some slight modification of such a reaction. The nature of the process leading to branching need not be so particularly specified, the essential condition being that in a branching collision two carriers of one type (OH) are produced from one of the other type (H). If this happens once (on the average) before the chain is terminated, the chain length will increase indefinitely and explosion ensue. But with H_2-N_2O there is no possibility of such an occurrence with H atoms or with OH radicals. In the H_2-O_2 reaction branching becomes possible because the oxygen molecule is diatomic; it is the splitting of this into two parts which ultimately yields the two carriers requisite for branching. Nitrous oxide, on the other hand, has only one atom available and cannot therefore give rise to two OH radicals even in a ternary collision such as $H + N_2O + N_2O$.

Although a very definite mechanism for the H_2-O_2 reaction has been adopted, which perhaps is not correct in detail, it will be of importance to find if homogeneous reactions between nitrous oxide and simple combustible molecules do exhibit well-defined lower and especially upper limits for explosion. If they do not, then the following statement would appear to sum up the behaviour of these reactions: In combustion processes involving nitrous oxide, branching chains and therefore chain explosion limits do not occur. The lower limits observed are due to thermal explosions, initiated homogeneously or heterogeneously, of a type similar to those discussed by Semenoff* some time ago. The reaction must, of course, take place under such conditions that these phenomena are usually observed. For instance, the mixture should be capable of propagating chains; the chain length should increase at low pressures and decrease at high pressures. These conditions can be realized with H_2-N_2O, but no sharp limits are observed. The sharpness of a limit may be masked by the occurrence of a relatively fast reaction outside the explosion region, such as occurs with H_2-O_2-NO_2 mixtures.†

The Photochemical Low Pressure Reaction

To eliminate the possibility of thermal initiation, the experiments recorded in Table I were made at low temperatures, using the mercury lamp with mer-

* 'Z. Physik,' vol. 48, p. 571 (1928).

† Norrish and Griffiths, 'Proc. Roy. Soc.,' A, vol. 139, p. 147 (1933).

cury vapour present in the reaction tube. In Table II the oxygen content of the mixture was varied, maintaining the total pressure unaltered. It will be observed that oxygen accelerates the reaction from 340 to 600° C, but the increase does not change much with temperature, the ratio of the rates increasing 50% for a 20-fold increase in the rate. The energies of activation of the two reactions $H + N_2O = OH + N_2$ and $H + O_2 + H_2 = H_2O + OH$ must therefore be nearly equal. If the values of R in Table II be plotted against the percentage of O_2 in the gas, a linear relation is obtained up to 33%.

Table I—5 cm tube. Composition of mixture 19·5 mm O_2, 300 mm of H_2 and of N_2O

Temperature ° C	340	400	460	525	600
Initial pressure	15·95	16·00	17·67	18·24	19·68
Rate	0·26	0·52	0·92	2·50	7·0
Rate (O_2-free)	0·115	0·23	0·41	0·92	2·20
R_{O_2}/R.....	2·25	2·3	2·3	2·7	3·2

Table II—Temperature 390° C

Composition of mixture	O_2	—	10	20	40	100	100
	H_2	100	100	100	100	100	100
	N_2O	100	100	100	100	100	—
	O_2%	0	4·8	9·1	16·6	33·3	50
Pressure		16·00	16·33	16·00	16·23	16·12	16·12
Rate		0·330	1·05	1·97	3·75	8·40	6·30

Small quantities of a foreign gas can exert a large influence on a chain reaction only by destroying the carriers before they would normally end, or by increasing the rate of initiation. It is improbable, in the present work, that O_2 molecules affect the rate of starting, for the quenching radius of O_2 is only twice as great as that of H_2.* The acceleration will therefore be due to the participation of oxygen in the propagation reactions.

Two possibilities may be distinguished:

(*a*)	$H + H_2 + O_2 = H_2O + OH$	k_{10}
(*b*)	$H + O_2 = HO_2$	k_{11}
	$HO_2 + H_2 = H_2O + OH$	k_{12}
	$HO_2 + N_2O = H + N_2O + O_2$	k_{13}
	$HO_2 = H + O_2$	k_{14}

* Zemanski, 'Phy. Rev.,' vol. 36, p. 919 (1930).

(*a*) will be considered first. The stationary concentrations of H and of OH will be given by the equations

$$\frac{d[H]}{dt} = I + k_5[OH][H_2] - k_4[H][N_2O] - k_{10}[H][H_2][O_2] - k_9[H] = 0,$$

$$\frac{d[OH]}{dt} = k_4[H][N_2O] + k_{10}[H][H_2][O_2] - k_5[OH][H_2] - k'_9[OH] = 0,$$

whence

$$\frac{d[H_2O]}{dt} = \{k_4[N_2O] + k_{10}[H_2][O_2]\} I/k_9.$$

There are difficulties in accepting this simple scheme, for it would be expected that a triple collision with an energy of activation similar to that of $H + N_2O$ would occur much less frequently than the latter reaction, whereas in fact, the rate of removal of H atoms by O_2 is faster than that by N_2O. By postulating the formation of the complex, HO_2, this difficulty can, in part, be overcome. For (*b*), therefore,

$$\frac{d[HO_2]}{dt} = k_{11}[H][O_2] - k_{12}[HO_2][H_2] - k_{13}[HO_2][N_2O] - k_{14}[HO_2] = 0,$$

$$[HO_2] = \frac{k_{11}[H][O_2]}{k_{12}[H_2] + k_{13}[N_2O] + k_{14}}.$$

$$\frac{d[H]}{dt} = I + k_5[OH][H_2] - k_4[H][N_2O] - k_{11}[H][O_2] - k_9[H] = 0,$$

$$\frac{d[OH]}{dt} = k_4[H][N_2O] + k_{12}[HO_2][H_2] - k_5[OH][H_2] - k'_9[OH] = 0,$$

$$\frac{d[H_2O]}{dt} = \left\{k_4[N_2O] + \frac{k_{11}[O_2] \cdot k_{12}[H_2]}{k_{12}[H_2] + k_{13}[N_2O] + k_{14}}\right\} I/k_9.$$

If k_{13} and k_{14} are small compared with k_{12} then

$$\frac{d[H_2O]}{dt} = \{k_4[N_2O] + k_{11}[O_2]\} I/k_9.$$

This equation is in agreement with experiment in that the rate should increase linearly with $[O_2]$. At 390° the ratio $k_{11}/k_4 = 13{\cdot}3$. Oxygen molecules increase the rate of production of water by reaction with the atomic hydrogen of the H_2-N_2O chains. At higher temperatures, the combination of H_2 and O_2 may also increase the rate of initiation.

High Pressure Thermal Reaction

Having established that oxygen can affect the propagation, the next question is whether the homogeneous or heterogeneous combination of hydrogen and oxygen may give rise to molecules or atoms capable of initiating chains in hydrogen-nitrous oxide. First of all, experiments were made on the effect of O_2 on the thermal reaction ; the results are given in Table III. The mixtures

Table III—1·7 cm tube. Temperature 585° C

% O_2	4·75	2·37	1·18	0·59	0·0
Total pressure	100·5	103·0	99·0	100·0	99·0
Rate	15·0	6·0	3·8	1·75	0·26

were made up separately in a gas holder before admission to the reaction bulb. As might be expected, oxygen considerably increases the rate, which may, of course, be due to the propagation. Examination of the values of Δp (not given) will not, however, sustain this explanation entirely. Comparison of the experimental with the calculated values of Δp indicated that hydrogen and oxygen do react to yield H or OH which then start off the chains. In order to find whether this additional source of carriers is due to a wall or to a homogeneous process, the kinetics of the reaction were further investigated with respect to $[N_2O]$, $[H_2]$ and packing. R is directly proportional to $[O_2]$, as may be seen if the results are plotted. Hydrogen and nitrous oxide are inhibitors, for the initial rate of reaction is very nearly independent of pressure, as is shown in fig. 1, where $\Delta p - t$ curves are plotted for a mixture containing 3·3% oxygen. One prominent point is that the curves bend round comparatively rapidly, especially at low pressures, long before the reaction has gone to completion. The oxygen must therefore be consumed in the initial stages. To investigate the individual effects of hydrogen and of nitrous oxide, the following procedure was adopted : p_{N_2O} was fixed at 50 mm, p_{O_2} at 2·4 mm, and p_{H_2} was varied within measurable limits. A similar set of experiments was made with $p_{N_2O} = 150$ mm. A third series was carried out in which p_{H_2} and p_{O_2} were respectively 50 and 2·6 mm, and p_{N_2O} was varied. The results are summarized in Table IV where it will be observed that hydrogen and nitrous oxide exert about the same inhibitory action. The approximate constancy of $R \cdot p_{H_2}^{\frac{1}{2}}$ and $R \cdot p_{N_2O}^{\frac{1}{2}}$ shows that the rate is inversely proportional to the square root of the pressure, but when the pressure of nitrous oxide is considerably greater than that of hydrogen, the latter ceases to have any effect.

Table IV—5 cm bulb. Temperature 568° C

p_{N_2O}	p_{O_2}	p_{H_2}	R	$Rp_{H_2}^{\frac{1}{2}}$
48·2	2·4	24·2	15·0	7·5
48·2	2·4	50·0	11·4	8·1
48·2	2·4	100·2	7·2	7·3
48·4	2·4	199·8	4·6	6·5
48·0	2·4	299·6	4·0	6·9
140·0	7·0	150·0	5·6	6·9
138·6	7·0	100·4	5·6	5·6
143·2	7·0	50·0	6·6	4·6
141·1	7·1	25·0	6·0	3·0
				$Rp_{N_2O}^{\frac{1}{2}}$
199·5	2·6	48·5	2·1	3·0
148·7	2·7	48·7	2·8	3·4
99·1	2·7	49·1	3·6	3·6
48·4	2·7	48·4	5·2	3·6

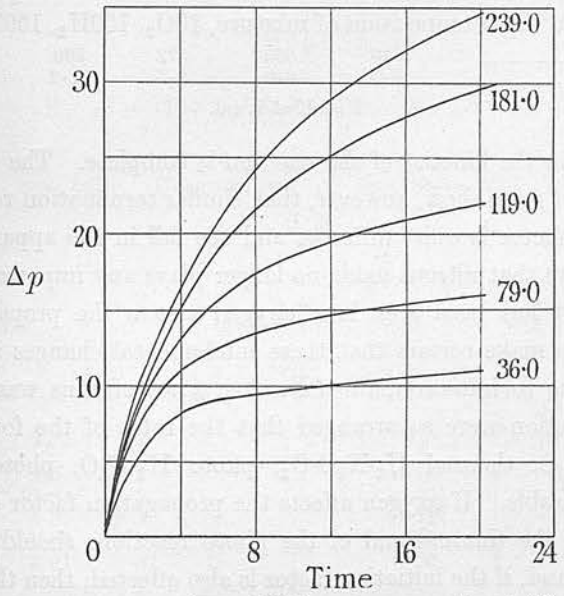

FIG. 1—Effect of total pressure, thermal high pressure reaction, 3·3% oxygen, temperature 532° C

Argon does not cause any inhibition when added to the extent of 200 mm to 100 mm of H_2-O_2-N_2O mixture. Packing experiments were also made to determine the nature of chain termination, using exactly the same tube and packing material as employed in the thermal high pressure experiments (Part I, p. 532). For comparison, the results are given in full in Table V. A decrease of 50% occurs in the rate, which is the same as that found for O_2-free mixtures.

Table V—2·5 cm tube. Packing 0·7 cm tubes. Temperature 640° C. Composition of mixture, $10O_2$, $250H_2$, $250N_2O$. Total pressure 100 mm

	Packed		Empty	
t	Δp	Δp	Δp	Δp
1	5·5	6·5	12·0	11·5
2	10·0	12·0	21·5	20·5
3	13·5	15·0	28·0	27·0
4	17·0	19·0	33·0	32·0
6	21·0	23·5	40·0	38·5
8	24·5	26·0	42·0	41·0
10	26·0	28·0	43·5	—

Since the discussion of the temperature coefficients of the different reactions has shown that there may be a possibility of assigning separate values to the various steps in the reaction, measurements were made of the apparent energy of activation of the present reaction, Table VI.

Table VI—Composition of mixture, $10O_2$, $150H_2$, $150N_2O$

Temperature ° C	510	555	572	590	606	649
Rate	2·9	6·0	8·5	11·2	13·7	20·5

$E = 17·4$ k. cal.

The change in the kinetics of the reaction is complete. The effect of packing and of inert gases show, however, that similar termination reactions occur. The initiation factor is quite different and the fall in the apparent energy of activation shows that nitrous oxide no longer plays any important part in the first stages. It has been seen how oxygen affects the propagation factor, and in order to make certain that these fundamental changes in the kinetics were partly due to initiation, the following series of runs was made. Conditions for reaction were so arranged that the rates of the four reactions—thermal H_2-N_2O, thermal H_2-N_2O-O_2, photo H_2-N_2O, photo H_2-N_2O-O_2, were all comparable. If oxygen affects the propagation factor only, then the acceleration of the thermal and of the photo reactions should be the same. On the other hand, if the initiation factor is also affected, then the acceleration of the photo reaction will be somewhat smaller than that of the thermal. The reasons for these statements can be readily seen if the general velocity equations are set down for the four conditions:

$$R_T = P_T \cdot I_T^{\frac{1}{2}},* \quad (1)$$

$$R_{T,O_2} = (P_T + P_{O_2})(I_T + I_{O_2})^{\frac{1}{2}}, \quad (2)$$

$${}_PR_T = P_T \cdot (I_T + I_P)^{\frac{1}{2}}, \quad (3)$$

$${}_PR_{T,O_2} = (P_T + P_{O_2})(I_T + I_{O_2} + I_P)^{\frac{1}{2}}. \quad (4)$$

* The termination factors are identical for all four reactions, and for simplicity are not inserted in the equations.

If $I_{O_2} = 0$,

$$R_{TO_2} - R_T = {}_PR_{T,\,O_2} - {}_PR_T.$$

If $I_{O_2} \neq 0$ and $I_T \doteqdot I_{O_2} \doteqdot I_P$,

$$R_{T,\,O_2} - R_T > {}_PR_T - {}_PR_{T,\,O_2}.$$

P and I are propagation and initiation factors. The suffixes T, O_2, P refer respectively to the thermal, the O_2, and the photo reactions. From these equations, the relative values of I_T, I_{O_2}, and I_P may be calculated. Let $P_{O_2} = \alpha P_T$, α can be computed from the oxygen content of the mixture and the results in Table VII. Equations (1) and (3) yield

$$I_T = I_P \{R_T^2/({}_PR_T^2 - R_T^2)\},$$

and (1), (2), (3), and (4) give

$$I_{O_2} = I_P \left(\frac{a+b}{a-b}\right),$$

where $a = {}_PR_{T,\,O_2}^2 - (1+\alpha)^2 R_T^2$ and $b = R_{T,\,O_2}^2 - (1+\alpha)^2 R_T^2$.

Table VII—5 cm tube. Composition of mixture, $5O_2$, $247H_2$, $247N_2O$. $\alpha = 0{\cdot}30$

Temp. °C	Pressure	R_T	$R_{T,\,O_2}$	${}_PR_T$	${}_PR_{T,\,O_2}$	$(R_{T,\,O_2} - R_T)$	$({}_PR_{T,\,O_2} - {}_PR_T)$
550	100	0·60	2·75	1·95	3·45	2·15	1·50
578	50	0·70	4·36	2·40	5·00	3·56	2·6
572	100	1·05	4·20	3·3	5·9	3·15	2·6
572	150	1·96	4·9	3·2	6·0	3·0	2·8
618	100	3·4	8·7	5·9	10·5	5·3	4·6

I_T :	I_P :	I_{O_2}	I_T :	I_P :	I_{O_2}
1	9·6	11·7	0·14	1	1·22
1	10·6	21·9	0·095	1	2·07
1	8·9	8·9	0·112	1	1·00
1	1·66	2·60	0·60	1	1·57
1	2·01	2·87	0·50	1	1·43

The results for a few different pressures and temperatures are collected in Table VII. The acceleration of the two reactions is not equal, as will be observed from an examination of columns 7 and 8. This is more clearly shown by the calculations on the relative magnitudes of I. In the first set, $I_T = 1$ and in the second $I_P = 1$. I_P is nearly independent of temperature and pressure and hence the variation of the other quantities is given in better perspective. The second set of calculations demonstrates that the thermal reaction, compared with the photo, is greater as the temperature and pressure increase. The first shows that initiation by oxygen is of greatest importance

at low pressures and temperatures. This is in accordance with the value of E for the oxygen reaction being smaller than E for the normal reaction. Furthermore, since it has been found that the temperature coefficients of the propagation factors are nearly the same, the effect of packing is identical and there is initiation by O_2, it must be concluded that, under these conditions, the initiation reaction involves both H_2 and O_2 and takes place in the gas phase with an energy of activation considerably less than that for the decomposition of nitrous oxide.

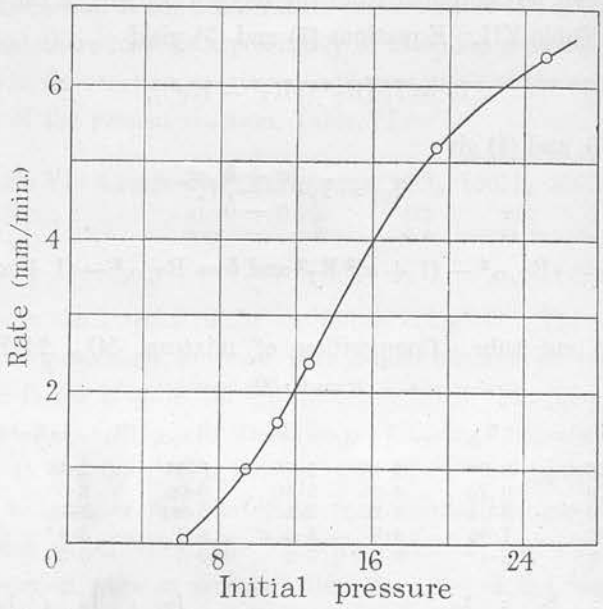

FIG. 2—Effect of total pressure, thermal low pressure reaction, temperature 602° C, 2·91% oxygen

The Low Pressure Reaction

It has been mentioned previously that, above 50 mm the pressure of a given H_2-N_2O-O_2 mixture does not affect the initial rate. As the pressure is reduced below this value, the rate diminishes linearly as is indicated by fig. 2. The curve does not pass through the origin, but makes an intercept on the pressure axis. The reaction velocity would thus appear to drop to a very small value when the pressure is below a certain critical point, in the present instance, 8 mm. If the individual runs are examined, it is found that Δp increases quite rapidly at first, but later changes only very slowly, although the reaction has not proceeded to completion. For example, with an initial pressure of 19·4 mm, Δp is almost steady after attaining 4 mm, which is equivalent to 40% of the

total possible increase. Had the observed value of Δp been due to the H_2-O_2 reaction alone, the pressure decrease would have been 0·6 mm. The comparatively abrupt bending over of the $\Delta p - t$ curves is due to the pressure of the mixture falling below the critical value. An essentially similar phenomenon is obtained when the oxygen content of a $1 : 1H_2$-N_2O mixture at constant pressure is altered (Table VIII). Above 12·5% O_2, the reaction is rapid and increases if the oxygen percentage is raised to 5. At 0·63%, however, the rate has dropped to a very small value. On raising the temperature to 650°, a conveniently measurable velocity is obtained, which does not greatly depend on the oxygen content and is, indeed, not much faster than that for the oxygen-free gases.

Table VIII

Temp. ° C	570		570		570		560	
% O_2	5		1·25		0·63		0·63	
Pressure	12·80		13·06		12·84		12·80	
	t	Δp	t	Δp	t	Δp	t	Δp
	0·25	2·25	0·25	0·46	0·5	0·00	0·5	0·38
	0·50	3·46	0·50	0·76	2	0·04	1	0·62
	0·75	4·16	0·75	0·88	4	0·06	2	1·00
	1·0	4·44	1	1·02			3	1·30
	1·25	4·54	1·5	1·36			4	1·56
	1·75	4·82	2	1·54			6	1·88
			3	1·82			8	2·10
			6	2·06			10	2·30

Temp. ° C	650		650		650	
% O_2	0·31		0·16		—	
Pressure	12·71		12·98		12·80	
	t	Δp	t	Δp	t	Δp
	1	0·26	1·5	0·38	1	0·20
	2	0·56	3	0·70	2	0·38
	4	0·96	4	0·80	4	0·80
	6	1·28	7	1·40	6	1·04
	8	1·60	10	1·78	10	1·62
	10	1·88	15	2·36	14	2·16
	15	2·36	21	2·78		
	20	2·78				

If the $\Delta p - t$ curves are plotted, the same tendency to bend over is not so marked at 650°. The oxygen pressure would thus seem to control the position of the critical point. If the reaction above the critical pressure is to be identified with that at high pressures, it would be expected that, as with O_2-free gases, the apparent energy of activation would decrease with pressure. This is borne out by the data in Table IX, where it will also be noted that, for a given mixture at a constant pressure, there is a critical value for the temperature, below which the rate is slow.

Table IX—Composition $12O_2$, $200N_2O$, $200H_2$. Pressure 12·8 mm
5 cm tube

Temperature ° C	510	519	525	540	580	625
Rate	0·01	0·95	1·25	2·05	3·3	8·2

$E = 30·6$ k. cal.

Finally, packing experiments show clearly the importance of inhibition by walls. For example, in the 5-cm tube at 550° with a mixture containing 2·9% O_2, the critical pressure was 6 mm, the rates at 7·67 and 20·10 mm being respectively 1·00 and 2·40 mm/min. On packing the tube completely with

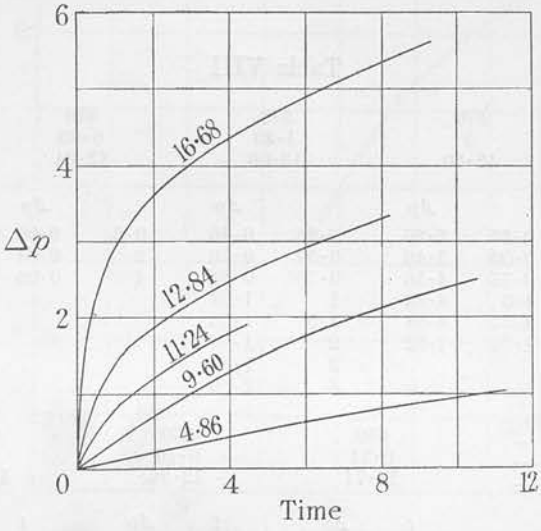

FIG. 3—Effect of total pressure, packed reaction bulb. Temperature 710° C, 2·9% O_2

0·7 cm tubes, no measurable reaction occurred at all and the temperature had to be raised to 710° to get a conveniently observable rate, which for a pressure of 16 mm was 1·55 mm/min. The rate of the H_2-N_2O reaction was now 0·50 mm/min. In the packed tube, however, there was still evidence of the existence of a critical pressure, for it will be seen from fig. 3, where $\Delta p - t$ curves are plotted for different total pressures, the form of the curves changes between 9·60 and 11·24 mm. This is brought out more clearly in Table X where a comparison is shown for an O_2-free and an O_2-containing mixture at 16·00 and at 8 mm, *i.e.*, above and below the critical pressure. The acceleration of the reaction is much greater at 16 than at 8 mm.

It should be mentioned that, in all these experiments, the mixtures were made up previously in a separate gas holder, for it was neither convenient nor

accurate to add small amounts of oxygen to the H_2-N_2O mixture. A considerable number of experiments was carried out in which the gases were added separately to the bulb and the important observation was made that, if only hydrogen and oxygen were admitted without nitrous oxide, there was immediate explosion and the pressure fell extremely rapidly. This occurred with pressures and temperatures above the critical values for the H_2-N_2O-O_2 reaction.

Table X—Composition of mixture as in Table IX

Above transition point				Below transition point			
		O_2 free				O_2 free	
p 16·04		16·24		8·06		8·00	
t	Δp	t	Δp	t	Δp	t	Δp
0·5	1·64	1	0·40	0·5	0·09	0·5	0·03
1·1	2·60	2	0·84	1	0·26	1	0·21
2·1	3·24	4	1·74	2	0·59	2	0·36
4	3·94	6	2·46	3	0·85	3	0·53
6	4·54	8	3·02	5	1·26	5	0·83
8	5·04	10	3·44	7·5	1·65	7·5	1·17
R_0 3·30		R 0·42		R_0 0·295		R 0·175	
$R_0/R = 7·9$				$R_0/R = 1·69$			

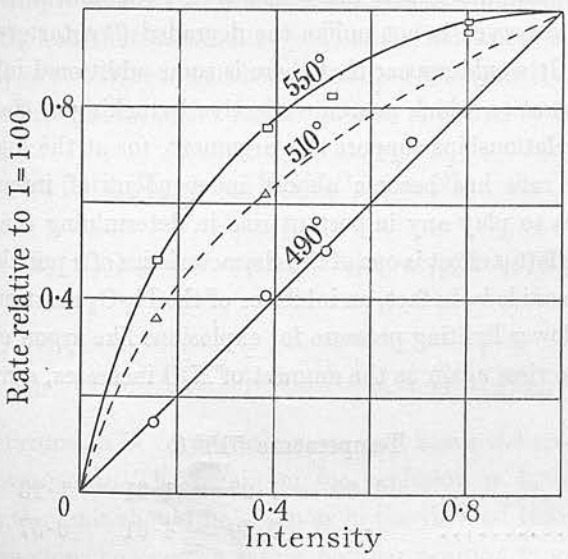

FIG. 4

The unusual character of the reaction is further borne out by experiments on the effect of the intensity of the light in the photochemical reaction in the region of the transition point. The rate-intensity curves are given in fig. 4 for three temperatures. The dark reactions were not greater than 5% of the total. At 492°, a linear relation is obtained as might be expected, but at 510°

and still more so at 550°, curvature is marked in such a way as to indicate that the exponent of I at 510° is 0·5 and even less at 550° for the dotted curve refers to $R \sim I^{\frac{1}{2}}$. The interpretation of the results at 510° might simply be that the increase in rate has altered the termination process from a wall to a gas phase reaction. Although this may in part be true, the fact that at 550°, $R \sim I^{1/n}$ where $n > 2$ and that in the ordinary photo reaction, H_2-N_2O, at a rate of the order of 1 mm per minute surface termination is still predominant, shows that this explanation is not sufficient.

Discussion of the Mechanism

The critical point observed in the low pressure O_2-reaction bears a remarkable similarity to the lower limit in H_2-O_2 mixtures. The reaction above this point is not, however, an explosion, for it was quite easy to get spontaneous inflammation at low pressures if the temperature was raised sufficiently. Since the H_2-O_2 mixture itself is spontaneously explosive and, above the critical point initiation is largely due to the H_2-O_2 reaction, it may be that the stable reaction observed is not unlike the degraded (" entartete ") explosions of Semenoff.* It would appear that there is some additional inhibition factor coming into operation which prevents effective branching of the chains. The intensity-rate relationships support this argument, for at the highest temperature 550°, the rate has become almost independent of intensity; that is, initiation ceases to play any important role in determining the course of the reaction. This latter effect is one of the characteristics of a pure lower explosion limit. Nitrous oxide is, in fact, an inhibitor of the H_2-O_2 reaction for, although it reduces the lower limiting pressure for explosions like argon or helium,† the critical pressure rises again as the amount of N_2O increases, *e.g.*,

Temperature 515° C

$p_{H_2+O_2}$	1·60	1·27	1·21	1·23	1·61
p_{N_2O}	—	3·20	4·81	6·57	9·61

The limit was determined by admitting a 2 : 1 H_2-O_2 mixture until inflammation was observed. A short time was allowed for the water formed in the explosion to be withdrawn by the P_2O_5, when the residual pressure was noted. Nitrous oxide was then added and the foregoing procedure repeated.

* 'Z. phys. Chem.,' B, vol. 2, p. 464 (1931).

† Hinshelwood and Moelwyn-Hughes, 'Proc. Roy. Soc.,' A, vol. 138, p. 311 (1932).

Some curious observations were made during these experiments. If the H_2-O_2 mixture was quickly admitted to the tube and the lower limit passed, a much more violent explosion occurred at about 10 mm, which was accompanied by rapid vibration of the manometer pointer. If the flow of hydrogen and oxygen was arrested, the pressure fell very quickly as the water was removed. During this period, successive explosions were observed in the reaction tube, resembling those obtained with P_4-O_2 mixtures when the lower limit is passed. There may be some connection between these two types of explosion and the experiments of Ouellet* who used a quantum counter for investigating the lower limit of the P_4-O_2 reaction. In these, the lower limit was succeeded at a higher pressure by another explosion with a flash of a different colour, which alone affected the counter (it may be noted that the counter was only sensitive to radiation of $\lambda < 280\ m\mu$) and hence it was concluded that there were two kinds of explosion in so far as the nature of the chemiluminescence was concerned.

The modification of the previous theory of the effect of oxygen to allow for branching is simply made. It will be assumed that branching occurs in the step $HO_2 + H_2$ and that as usual $(\alpha - 1)$ is the efficiency of branching, *i.e.*, the probability of two OH radicals being produced when one H atom disappears. The equations for the stationary concentrations of H and of OH are therefore

$$\frac{d[H]}{dt} = I + k_5[OH][H_2] - k_4[H][N_2O] - k_9[H] - k_{11}[H][O_2] = 0,$$

$$\frac{d[OH]}{dt} = I + k_4[H][N_2O] - k_5[OH][H_2] + \alpha k_{11}[HO_2][H_2] = 0,$$

whence

$$\frac{d[H_2O]}{dt} = \{k_4[N_2O] + k_{11}[O_2]\}\frac{I}{k_9 + (1-\alpha)k_{11}[O_2]}.$$

At low temperatures, α is very nearly unity and hence the second term in the denominator vanishes. The condition for explosion is $k_9 = (\alpha - 1)k_{11}[O_2]$ and therefore the limit should be sharp as in the thermal H_2-O_2 reaction. In the present reaction, however, a rather peculiar position arises. It has been seen that there is a little gas phase termination in the low pressure reaction. If the stationary concentration of H or of OH be raised much above that obtaining under the conditions employed in these experiments, for example, by a branching mechanism, gas phase termination will become of ever-increasing importance. The functioning of this additional inhibitory factor may, at any

* 'Trans. Faraday Soc.,' vol. 29, p. 486 (1933).

rate in a small region, prevent effective branching and thus allow the stable reaction to be measured. The transition point is therefore reached when [H] attains a certain value, which will naturally be affected by packing, temperature, and oxygen content of the mixture, in a somewhat similar manner to a lower limit. At high pressures gas termination is so important that a sharp transition is not obtained ; likewise, when the chains are short, as in a packed tube, transitional characteristics are only slightly in evidence.

On p. 762 it was shown that although oxygen is more effective than N_2O in producing OH radicals from a hydrogen atom, yet the energies of activation of the two reactions are almost identical. First of all, this rules out the possibility of the simple reaction $H + H_2 + O_2 = H_2O + OH$ since, if such a ternary collision required the same energy of activation as $H + N_2O$, the probability of its happening would be extremely small. Recently, L. Farkas* has measured the rate at which H atoms are removed in a mixture of H_2 and O_2 at room temperature and found that the velocity was about 1/50 of that calculated from the number of ternary collisions $H + H_2 + O_2$, and is not changed by temperature. This discrepancy can be explained by supposing that the removal of an H atom is not accompanied by the production of OH. This latter process requires as much activation as the reaction $H + N_2O$. But the oxygen molecule is more effective than the N_2O molecule in yielding OH, and therefore the rate of $HO_2 + H_2 = H_2O + OH$, athough possessing the same energy of activation, is faster than $H + N_2O = OH + N_2$. The concentration of HO_2 must consequently be greater than that of H ; from the results in Table I, the order of magnitude is 10.

The author desires to thank Dr. E. B. Ludlam and Professor J. Kendall for their continued help and encouragement throughout the course of this work, which was carried out in the Chemistry Department of the University of Edinburgh and subsequently at the Department of Colloid Science of the University of Cambridge. He also thanks the Royal Commissioners of the Exhibition of 1851 for a Senior Studentship.

Summary

The effect of the addition of oxygen on the kinetics of the hydrogen-nitrous oxide reaction has been investigated in order to compare the H_2-N_2O and H_2-O_2 reactions under similar conditions.

* Private Communication.

Summary of Reactions

...ction	Kinetic equation (observed) R ~	Kinetic equation (calculated)‖ R ~	E (total)	E (initiation)
...al high ...sure	$[N_2O]\,[H_2]^{0\cdot5}$*	$[N_2O]\sqrt{\frac{[N_2O]\,([N_2O]+[H_2])}{([N_2O]+[H_2])}}$	36·5	57
...al low ...sure	$[N_2O]^2\,[H_2]^{0\cdot5}$*	$[N_2O]^2\,([N_2O]+[H_2])$	49·5	50
...high ...sure	$I^{\frac{1}{2}}$	$[N_2O]\sqrt{\frac{[H_2]}{([N_2O]+[H_2])^2}}\,I^{\frac{1}{2}}$	<36	0
...low ...sure	$[N_2O][H_2]^{0}\,I$	$[N_2O]\cdot\frac{[H_2]}{[N_2O]+[H_2]}\cdot I$	14	0
...al high ... + O_2	$[O_2]\,.\,[N_2O]^{-0\cdot5}\,.\,[H_2]^{-0\cdot5}$	$([N_2O]+\alpha[O_2])\sqrt{\frac{?}{([N_2O]+[H_2])}}$	17	<57
...al low ... + O_2	$[O_2]$	$([N_2O]+\alpha[O_2])\sqrt{?}$	31‡	<50
...high ... + O_2	—	$([N_2O]+\alpha[O_2])\sqrt{\frac{[H_2]}{([N_2O]+[H_2])^2}}$	<17§	0
...low ... + O_2	$[O_2]\,.\,I^{(1\to0)}$†	$([N_2O]+\alpha[O_2])\cdot\frac{[H_2]}{[N_2O]+[H_2]}$	14	0

* These exponents are to some extent a function of $[N_2O]$.
† Exponent depends on temperature.
‡ Measured above the transition point.
§ Estimated from the data in Table VII.
‖ The coefficients for [H] and $[N_2O]$ are not inserted.

The thermal and mercury photosensitized reactions have been studied in the pressure range 1–300 mm.

At high pressures, the addition of small quantities of oxygen increases the velocity, the kinetics change entirely and the energy of activation falls off. By using photochemical methods it is shown that oxygen participates in the initiation and in the propagation of the chains. From packing experiments it is also shown that initiation is homogeneous.

At low pressures in the thermal reaction, a transition point is observed above which the reaction is comparatively rapid and below which it is slow, provided wide bulbs are used. This point depends on the oxygen content and the temperature of the gases; it is displaced to higher temperatures on packing the reaction tube. The phenomenon has some definite connection with the lower limit of the H_2-O_2 reaction. Photo experiments confirm these observations in that as the temperature is raised the value of the exponent n in the equation Rate = const. × (intensity)^n decreases from unity to almost zero.

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The Photochemical Oxidation of Phosphine above the Upper Explosion Limit

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The Photochemical Oxidation of Phosphine above the Upper Explosion Limit

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(Received June 27, 1934)

An investigation has been made of the kinetics of the photochemical oxidation of phosphine above the upper explosion limit. The results are summarized by the equations

Mercury sensitized reaction $-d[PH_3]/dt = \text{const.}\ [PH_3]/[O_2]^2 \times \text{intensity}.$

Direct photo-reaction $-d[PH_3]/dt = \text{const.}\ [PH_3]^2/[O_2]^2.$

The reactions are shown to be of the chain type and inhibited by oxygen. On the basis of previous knowledge of the propagation of the chains, the question of termination was examined and it is shown that out of six possible cases, only one is in agreement with the experimental facts. This is that the chain carrier, which normally reacts with phosphine, is destroyed in a ternary collision with two oxygen molecules or with one oxygen and one nitrogen molecule (or an argon atom). The efficiency of the collision is about 0.5. In view of these results, it is highly probable that this carrier is an oxygen atom. In the photosensitized reaction one-fifth of the collisions between oxygen molecules and excited mercury atoms results in the initiation of a chain. These results are shown to be quantitatively consistent with the shape and also the position of the upper limiting explosion curve, except that the limiting pressure is a little higher than that calculated by a strict application of the theory of branched chains. The upper limit is displaced to higher pressures by illumination of the mixture, a phenomenon not predicted by theory. The effect is of short duration, <2 sec. and it is not exhibited at the lower limit. The significance of this result is discussed in relation to the theory of the reaction.

THE introduction of the conception of branching chains and of the diffusion of chain carriers to the walls into the theory of thermal chain reactions has provided an acceptable picture of the mechanism of many oxidation reactions. While much experimental work has revealed the essential similarity underlying these reactions there are many corollaries to the theory which have yet to be explored in detail. The difficulty, in many cases, is experimental; in others, it is not at present quite certain whether factors not at all included in the chain theory prevent to some extent its rigorous application. For example, there is a possibility that sharp explosion limits may be due to causes other than simple branching of the reaction chains.

One of the corollaries is the following: It is postulated that the condition for explosion is that the product of the probabilities of branching and termination be equal to unity. The limits should consequently be independent of the rate of starting of the chains, provided that there is actually some reaction taking place.

A second is concerned with the mechanism of the reaction outside the explosion limits. In the quantitative application of the theory, expressions are derived which give the stationary concentration of the carriers for any pressure. It happens, however, that in the thermal reaction, the rate of starting is often so small that a stable reaction is never observed. Sometimes, the stable is masked by a relatively fast heterogeneous reaction.

The reaction between phosphine and oxygen is particularly well suited to answer some of these questions. Its mechanism is undoubtedly complicated, but the general chain features which it exhibits are in very good agreement with the theory. Moreover, it has the further advantage that the propagation collisions are nearly one hundred percent efficient and thus do not require any energy of activation.[1] The correlation between the kinetics below and at the lower limit has been fairly fully established.[1, 2] No experiments have, however, been carried out above the upper limit except a preliminary set[3] where a complete analysis was not attempted. Such an analysis was necessary in order to establish a relationship between the two conditions.

In this connection, curious results have been obtained by Grant and Hinshelwood[4] at the upper limit in the hydrogen-oxygen reaction.

* Senior Student, Exhibition of 1851.

[1] Melville, Proc. Roy. Soc. **A139**, 555 (1933).
[2] Dalton and Hinshelwood, Proc. Roy. Soc. **A125**, 294 (1929); Melville, ibid. **A138**, 374 (1932).
[3] Melville and Roxburgh, Nature **131**, 690 (1933).
[4] Grant and Hinshelwood, Proc. Roy. Soc. **A141**, 29 (1933).

The limit is apparently governed by some form of gas phase inhibition, for argon and helium lower the upper explosion pressure. Above the limit, however, there is a stable reaction in which the same gases accelerate the reaction rate showing that the chains now end on the walls. It was thought at first that two entirely different mechanisms were in operation, for obviously, one of the conditions for the appearance of an upper limit is that the chain length should increase with decreasing pressure, whereas the kinetics of the stable reaction indicated that the chain length probably increased with pressure. The explanation apparently is that the decrease in chain length is more than compensated for by the increase in the probability of branching as the pressure is reduced.

It was thought that instead of employing photochemical means of artificially increasing the rate of starting, the introduction of a hot filament might prove just as suitable and at the same time provide detailed information about the heterogeneous starting of chain reactions. Unfortunately, the reaction is almost wholly heterogeneous[5] and so photo-initiation had to be employed.

The Theory of the Stable Reactions

The theory has been worked out for the kinetics at the explosion limits[6] but to apply it to the stable reactions requires some modification. Before deriving the equations for a number of assumptions, it is necessary to examine the simplifications which were made in the original theory. It was assumed that both carriers X_O and X_P are equally well removed by collision with the walls and that the rates of reaction with phosphine and with oxygen, respectively, are the same. There is a considerable amount of evidence that these assumptions are sufficiently exact for the purposes of calculation. For example, the theoretical and observed chain lengths below the lower limit are in good agreement, and the second postulate must be nearly true. If one carrier were more easily destroyed than the other, then it can easily be shown that the lower explosion limit equation would be

$$[PH_3]\{[PH_3]+[O_2]\}=\text{const.} \quad (1)$$

or

$$[O_2]\{[PH_3]+[O_2]\}=\text{const.}, \quad (2)$$

which is not in so good accordance with experiment as the equation $[PH_3][O_2]=\text{const.}$ Below the lower limit, the stationary concentrations of the carriers are given by

$$d[X_O]/dt = I + k[X_P][O_2] + k[X_O][PH_3] - K[X_O] = 0, \quad (3)$$

$$d[X_P]/dt = k[X_O][PH_3] - k[X_P][O_2] - K[X_P] = 0 \quad (4)$$

and therefore

$$-d[PH_3]/dt = (k[PH_3][O_2]/K') \cdot I, \quad (5)$$

where $K = K'/([PH_3]+[O_2])$, K being a constant and I the rate of starting.

Above the upper limit, there are a number of ways in which X_O and X_P may be destroyed. One of the objects of this investigation is to determine the kinetics of the reaction in order that an unequivocal choice may be made from among the possible mechanisms, and further to see whether the mechanism so chosen is consistent simultaneously with the position and shape of the upper limit curve.

There are six possible ways whereby the carriers could be destroyed

1. $X_O + X$ (k_4),
2. $X_O + X_O + X$ (k_5),
3. $X_O + X + X$ (k_6),
4. $X_P + X$ (k_7),
5. $X_P + X_P + X$ (k_8),
6. $X_P + X + X$ (k_9).

k is the velocity coefficient and X is either PH_3 or O_2 or any other molecule which may have been added to the gas mixture. Three examples of each case will be worked out *viz.*, (*a*) mercury sensitized initiation; in addition to the dissociation of the PH_3 by $Hg(^3P_1)$, it may also happen that oxygen is activated in such a manner as to start chains, and there are therefore two equations for this kind of initiation, (*b*) direct photo-dissociation of the PH_3.

This procedure of examining each possibility is adopted in order to meet a criticism which is often advanced against the interpretation of kinetic results, namely, that two or more mechanisms may lead to the same equation. This occurs, in fact, in the present analysis, but fortunately there are means by which an unambiguous choice can be made.

[5] Melville and Roxburgh, J. Chem. Soc. 586 (1933); 264 (1934).

[6] See, e.g., Hinshelwood, *Kinetics*, 3rd edition, p. 264.

Case 1

The equations for $[X_O]$ and $[X_P]$ are

$$d[X_O]/dt = I + k[X_P][O_2] - k[X_O][PH_3] - k_4[X_O][X] = 0, \tag{6}$$

$$d[X_P]/dt = k[X_O][PH_3] - k[X_P][O_2] = 0. \tag{7}$$

For the mercury sensitized reaction, phosphine being dissociated

$$-\frac{d[PH_3]}{dt} = \frac{k[PH_3]}{k_4[O_2]} \cdot \frac{I_n[PH_3]}{[PH_3]+0.5[O_2]+0.37}. \tag{8}$$

The constant 0.37 (allowing for the radiation of resonance light) is calculated for the case where $[PH_3]$ and $[O_2]$ are expressed in mm of mercury, for a 2 cm tube and a mercury vapor pressure of 0.001 mm,[7] I_n is proportional to the intensity of the 253.7 mμ line from the mercury lamp. One important simplification can now be made. In the region above the upper limit where the phosphine pressure is low, that of the oxygen is so high that X in the above reaction scheme may be considered to be O_2. Eq. (8) can thus be simplified to

$$-d[PH_3]/dt = (k[PH_3]^2/k_4[O_2]^2) \cdot I_n. \tag{9}$$

For mercury sensitization with initiation by oxygen,

$$-\frac{d[PH_3]}{dt} = \frac{k[PH_3]}{k_4[O_2]} \cdot \frac{I_n \cdot \{A \cdot [O_2] \cdot 0.5 + [PH_3]\}}{[PH_3]+0.5[O_2]+0.37} = \frac{k[PH_3]}{k_4[O_2]} \cdot I_n, \tag{10}$$

where A is defined as the number of chains started per excited mercury atom which is deactivated by oxygen. For the direct dissociation,

$$-d[PH_3]/dt = (k[PH_3]^2/k_4[O_2])I_n. \tag{11}$$

Case 2

The last term in the equation for X_O will now be $-k_5[X_O]^2[X]$ and therefore

$$I = k_5[X_O]^2[X]. \tag{12}$$

Mercury sensitization (PH_3)

$$-\frac{d[PH_3]}{dt} = k[PH_3]\left\{\frac{[PH_3] \cdot I_n}{k_5[X]([PH_3]+0.5[O_2]+0.37)}\right\}^{\frac{1}{2}} = \frac{k[PH_3]^{\frac{3}{2}}}{[O_2]}\left(\frac{I_n}{k_5}\right)^{\frac{1}{2}}. \tag{13}$$

Mercury sensitization (O_2)

$$-d[PH_3]/dt = k[PH_3](I_n \cdot A/k_5[O_2])^{\frac{1}{2}}, \tag{14}$$

and the direct reaction

$$-d[PH_3]/dt = k[PH_3]^{\frac{3}{2}}(I_n/k_5[O_2])^{\frac{1}{2}}. \tag{15}$$

Case 3

The last term in the equation for $[X_O]$ is $k_6[X_O][X]^2$. Mercury sensitization (PH_3),

$$-\frac{d[PH_3]}{dt} = \frac{k[PH_3]}{k_6[X]^2} \cdot \frac{[PH_3] \cdot I_n}{[PH_3]+0.5[O_2]+0.37} = \frac{k[PH_3]^2 \cdot I_n}{k_6[O_2]^3}. \tag{16}$$

Mercury sensitization (O_2),

$$-d[PH_3]/dt = (k[PH_3]I_n \cdot A)/k_6[O_2]^2. \tag{17}$$

Direct reaction,

$$-d[PH_3]/dt = (k[PH_3]^2 \cdot I_n)/k_6[O_2]^2. \tag{18}$$

[7] Cf. Proc. Roy. Soc. **A138**, 385 (1932).

Cases 4, 5 and 6

The corresponding cases for X_P are obtained in exactly the same way. The last term in the X_0 equation is discarded, while an additional term is added to the X_P equation in order to express how this carrier is removed. This gives rise to the following nine equations.

$$\text{Case 4}\quad X_P+X\quad (k_7)\begin{cases}\text{Hg } (PH_3) & -d[PH_3]/dt=kI_n/k_7, & (19)\\ \text{Hg } (O_2) & -d[PH_3]/dt=k[O_2]\cdot A/k_7[PH_3], & (20)\\ \text{Direct} & -d[PH_3]/dt=k[O_2]/k_7. & (21)\end{cases}$$

$$\text{Case 5}\quad X_P+X_P+X\quad (k_8)\begin{cases}\text{Hg } (PH_3) & -d[PH_3]/dt=k([PH_3]\cdot I_n/k_8)^{\frac{1}{2}}, & (22)\\ \text{Hg } (O_2) & -d[PH_3]/dt=k(I_n\cdot A/k_8[O_2])^{\frac{1}{2}}, & (23)\\ \text{Direct} & -d[PH_3]/dt=k([O_2][PH_3]\cdot I_n/k_8)^{\frac{1}{2}}. & (24)\end{cases}$$

$$\text{Case 6}\quad X_P+X+X\quad (k_9)\begin{cases}\text{Hg } (PH_3) & -d[PH_3]/dt=k[PH_3]I_n/k_9[O_2]^2, & (25)\\ \text{Hg } (O_2) & -d[PH_3]/dt=k\cdot[PH_3]\cdot I_n/k_9[O_2], & (26)\\ \text{Direct} & -d[PH_3]/dt=k[PH_3]I_n/k_9[O_2]. & (27)\end{cases}$$

A possible objection might be raised against case 6, for $X=O_2$ and X_P+O_2 is a propagating collision. In presence of a third molecule, however, it is quite conceivable that a redistribution of energy occurs in such a way as to prevent the emergence of an X_0 molecule from the collision.

Experimental

Fig. 1 illustrates the essential parts of the apparatus. The main difficulty was to measure a change in phosphine pressure in presence of a large excess of oxygen. The apparatus was so arranged that it could readily be used for experiments on the upper limit. The silica reaction tube was placed in a water bath at 20°C fitted with a silica window. The source of the mercury line was a tungsten anode lamp L with a water-cooled cathode. A filter was employed to vary the intensity of the light and consisted of a solution of carbon tetrachloride in pure hexane.[8] A condensed spark between zinc disks rotating at right angles served as a light source for the experiments on the direct reaction. The input to the spark was about 0.2 amp. at 5000 volts, the distance between spark and reaction tube being 15 cm. Large pressures were measured by a capillary mercury manometer, smaller pressures by the spring gauge M_2 and low pressures by the oil manometer M_1, the position of the meniscus being read by a microscope. Apiezon oil A, thoroughly degassed, proved to be satisfactory. To increase the sensitivity, one of the limbs was made much wider than the other. Since this manometer was used differentially, it was also placed in a water bath. For the experiments at the upper limit, a steel needle valve was attached to the apparatus to regulate the rate of exhaustion of the explosion tube.

The procedure for the experiments on the stable reaction above the upper limit and at low phosphine pressures was as follows: Phosphine was admitted to R and to M_1, T being closed, and its pressure observed. T was opened and oxygen admitted, the pressure being now measured on

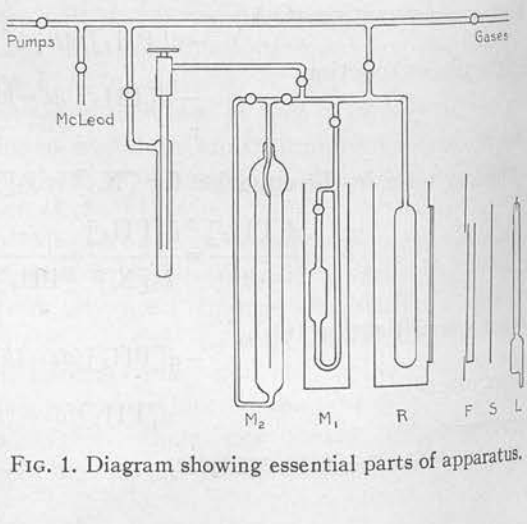

FIG. 1. Diagram showing essential parts of apparatus.

[8] Melville and Walls, Trans. Faraday Soc. **29**, 1255 (1933).

M_2, T was closed again and the shutter removed for a given time, after which the oil manometer was again read. This procedure was repeated for a number of exposures. In this manner, changes of pressure of 0.1 mm could be measured in presence of 30 mm of oxygen. Several blank experiments were made with oxygen alone to ensure that no spurious effects occurred, for instance, oxygen does dissolve in the oil, but since it was present at the same pressure in both limbs of the manometer and the runs were not prolonged, no appreciable change of oil level could be detected. The deposition of the phosphoric acid on the walls of the reaction did not appear to cut down the reaction velocity, for no increase in rate resulted when the tube was cleaned out. With excess of oxygen, the phosphine is practically completely oxidized to H_3PO_4, since the pressure decrease after the reaction had gone to completion amounted to nearly three times the pressure of the phosphine.

The preparation of mixtures above the upper limit was carried out in the usual way. The water bath surrounding the reaction vessel was removed and a small annular cup was fixed to R. Phosphine was passed in, liquid air poured into the cup and then the oxygen was added. When the liquid air had evaporated, the water bath was replaced and the apparatus allowed to stand for a few minutes until the pressure became steady, after which exhaustion and exposure were commenced.

The gases were prepared as described in previous papers.

Results

Photosensitized oxidation

It will be observed from an inspection of Eqs. (13)–(15) and (22)–(24) that the rate of oxidation for cases 2 and 5 should vary as the square root of the intensity, whereas in the other cases the relation is linear. Several possibilities can thus at once be eliminated if the intensity law is first of all investigated. Below the lower limit, the rate should, of course, be proportional to the intensity. The results (Table I) below the lower limit are in accordance with expectation and above the upper limit, there is no doubt that the rate is proportional to the first power of the intensity and therefore cases 2 and 5 may at once be eliminated. For a given pressure of phosphine, it is known from the experiments of Dalton and others[9] that by increasing the pressure of oxygen, the lower limit may be approached, or if the oxygen pressure be decreased, the upper limit is reached. The upper limit must, therefore, be due to oxygen participating in some reaction which is negligible at low pressures. When chain initiation is brought about by mercury sensitization, it is probable that oxygen molecules account for a number of the chains started and it is therefore necessary to evaluate the magnitude of the coefficient A defined on p. 741. In Fig. 2, $1/R$ and k^{-1} have been plotted against p_{O_2}, the dotted curve refers to the ideal case in which

TABLE I.

Intensity I	Init. Rate R (mm/min.)	R/I*	t for $\Delta p=0.525$ mm (min.)
Lower limit, $p_{PH_3}=0.254$ mm, $p_{O_2}=0.584$ mm			
1.00	0.072	0.072	0.85
0.15	0.012	0.072	5.20
0.68	0.053	0.072	1.05
0.38	0.028	0.065	2.00
1.00	0.083	0.072	0.70

Intensity	t for $\Delta p=0.064$	$t\times I$
Upper limit, $p_{PH_3}=0.127$ mm, $p_{O_2}=10.0$ mm		
0.38	1.65	0.63
0.68	0.90	0.61
1.00	0.55	0.55
0.15	3.70	0.56
0.51	1.24	0.63

* Corrected for the increase in the intensity during the series.

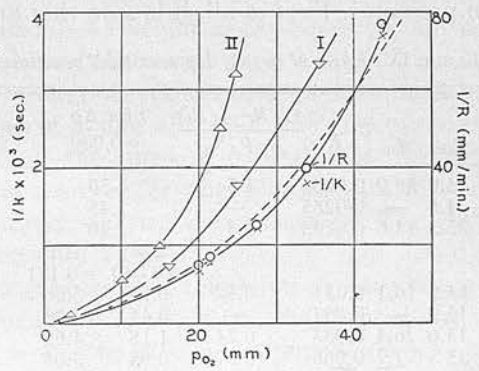

FIG. 2. Photosensitized reaction, curves I and II are for $p_{PH_3}=0.120$ mm and different intensities.

[9] Dalton and others, e.g., Proc. Roy. Soc. **A128**, 263 (1930).

TABLE II.

p_{PH_3}	0.261		0.261		0.261		0.261		0.261	
p_{O_2}	20.0		21.4		27.0		34.0		44.0	
t	Δp	$k\times10^3$ (sec.$^{-1}$)	Δp	$k\times10^3$ (sec.$^{-1}$)	Δp	$k\times10^3$ (sec.$^{-1}$)	Δp	$k\times10^3$ (sec.$^{-1}$)	Δp	$k\times10^3$ (sec.$^{-1}$)
0.25	0.017	1.54	0.016	1.22	0.009	—	—	—	0.001	—
0.50	0.033	1.41	0.029	1.30	0.021	0.92	0.012	—	—	—
0.75	—	—	.0430	1.23	0.029	0.81	0.017	0.51	—	—
1.00	0.066	1.51	0.055	1.19	0.041	0.92	0.025	0.52	—	—
1.50	0.092	1.40	0.079	1.23	0.056	0.84	0.042	0.61	0.016	—
2.00	0.118	1.73	0.097	1.09	0.073	0.81	0.047	0.54	0.026	0.26
3.00	0.162	1.28	—	—	0.104	0.78	0.071	0.54	0.035	0.26
4.00	—	—	—	—	—	—	0.094	0.54	0.055	0.29

$1/R$ and k vary as $p_{O_2}^2$. Table II contains the detailed runs and k is calculated assuming that $-d[PH_3]/dt=k[PH_3]$. The oxygen pressure may be regarded as constant during the reaction. Since these runs were not carried to completion, another series of experiments is given in Table III, where the pressure of oxygen was maintained

TABLE III. *Effect of phosphine.*

p_{PH_3}	0.260	0.190	0.129	0.132	0.066
p_{O_2}	9.4	10.5	9.2	10.0	10.0
Rate (R)	0.100	0.066	0.051	0.046	0.025
R/p_{PH_3}	0.038	0.035	0.039	0.035	0.038
$t(\Delta p=0.066)$	0.65	1.15	1.55	1.86	2.95
$t\times p_{PH_3}$	0.169	0.22	0.20	0.24	0.20

constant and that of phosphine varied. The constancy of R/p_{PH_3} and of $t\times p_{PH_3}$ shows that the rate is proportional to the pressure of the phosphine.

In Table IV, three series of results are listed for a constant oxygen pressure and for different argon pressures. First of all, it is seen that argon

TABLE IV. *Effect of argon. Hg sensitized reaction.*

p_{PH_3}	p_{O_2}	p_A	R	$(1/R-1/R_0)/p_A$*	t for Δp =0.039		k_{10}/k_6
0.260	25.0	55.0	0.0086	1.5	4.50		1.00
0.260	24.6	—	0.0285	—	1.45		—
0.263	25.7	14.6	0.0193	1.3	2.20		0.8
					Δp =0.039	Δp =0.131	
0.263	14.9	16.1	0.051	0.52	0.82	3.68	0.8
0.262	15.0	—	0.093	—	0.41	2.00	—
0.258	15.6	26.4	0.033	0.74	1.18	4.60	1.0
0.262	15.5	7.7	0.066	0.57	0.64	3.05	0.8
					$\Delta p=0.0655$		
0.261	14.6	44.9	0.0201	0.82	4.00		0.7
0.262	15.8	16.4	0.0283	1.00	2.47		0.9
0.261	15.8	—	0.0533	—	1.27		—

* R_0 is the rate in absence of inert gas.

inhibits the oxidation, although in comparison with oxygen it does not quench mercury resonance radiation. The inhibition must therefore be due to chain termination and since the value of $(1/R-1/R_0)/p_A$ is approximately constant, the inhibition term in the kinetic equation may be expressed in two ways *viz.*, $k_{10}[X_0][A]$ or $k_{11}[X_0][O_2][X]$.

Similarly, there is inhibition by nitrogen (Table V) and again according to the same law.

TABLE V. *Effect of nitrogen.*

Direct reaction, Zn spark
$p_{PH_3}=0.254$, $p_{O_2}=12$

p_{N_2}	12	26	18	6	0
t for $\Delta p=0.064$	2.62	3.84	3.37	1.62	1.17
k_{10}/k_6	1.2	1.1	1.2	0.80	—

Hg reaction, constant $p_{O_2}+p_{N_2}$

p_{PH_3}	p_{O_2}	p_{N_2}	R	t for $\Delta p=0.131$
0.262	39.0	—	0.066	2.22
0.256	11.0	32.0	0.074	2.16
0.271	20.4	20.3	0.104	1.47
0.259	10.8	30.5	0.131	1.06
0.271	26.7	13.3	0.090	1.75

Until a decision is made about the mechanism of termination, no calculation can be made of the coefficients k_{10} and k_{11}.

The kinetics of the reaction are, therefore, that

$$-d[PH_3]/dt=\text{const.}\ [PH_3]/[O_2]^2.$$

This does not decide the matter unequivocally, since case 3 and case 6 lead to the same equation if initiation in the first is due to oxygen and in the second to phosphine. Further, both cases allow the introduction of an inhibitory term containing oxygen, and argon and nitrogen. The inhibition by inert gases practically excludes cases 1 and 4

for it is probable, although the evidence is as yet indirect, that the chain carriers are not excited molecules of very short life and hence collision of X_O or X_P with argon or nitrogen should not lead to destruction.

Direct photo-oxidation

The number of mechanisms has now been reduced to two. Fortunately, the kinetic equations for the direct oxidation are quite different for cases 3 and 6 and thus it should be possible to decide which is the more probable. Intensity measurements were not considered to be necessary in view of the definite answer given by the photosensitised experiments. In Table VI the

TABLE VI. *Effect of phosphine.*

p_{PH_3}	p_{O_2}	t for $\Delta p=0.025$ (sec.)	$t\times p_{PH_3}^2$
0.130	17.3	108	18.2
0.535	17.7	7	20.0
0.275	17.4	26	19.7
0.131	17.2	85	14.6
0.391	17.3	10	15.3
0.261	17.3	20	13.6

complete data are given for varying oxygen and phosphine pressures. In Fig. 3, $1/R$ and t for $\Delta p=0.100$ mm have been plotted against $p_{O_2}^2$ and also against p_{O_2}, the pressure of PH_3 being 0.26 mm. The straight line obtained with the $p_{O_2}^2$ plot and also the constancy of the product $t\times p_{PH_3}^2$ in Table VI, indicates that the kinetics in this pressure range can be summarized by the equation,

$$-d[PH_3]/dt=\text{const. } [PH_3]^2/[O_2]^2.$$

Referring back to the theory given above, it will be observed that this equation only agrees with case 3 (18) and therefore the conclusion which may be drawn is that, above the upper limit, the chains are terminated by a triple collision between the chain carrier X_O, which normally reacts with phosphine, and with two oxygen molecules.

It is now possible to return to the question of inhibition by argon and nitrogen. The plots of $1/R$ against $p_{A(N_2)}$ are straight and hence the inhibition term will contain a factor $[N_2]$ or $[A]$. It is of importance to note that a quadratic term $[N_2]^2$ or $[A]^2$ need not be introduced. The most

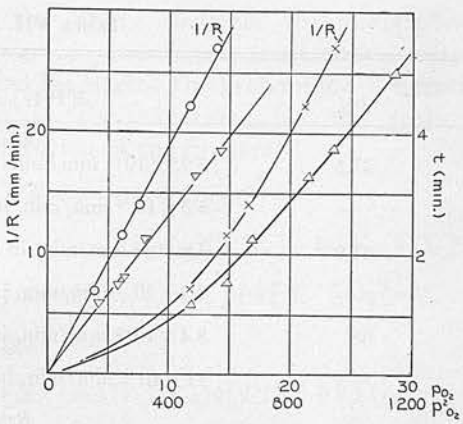

FIG. 3.

probable mechanism of the termination is that X_O must collide with a nitrogen molecule and an oxygen molecule. The function of the inert gas may simply be to stabilize the complex X_O+O_2 and thus prevent X_O further propagating the chain. Let the inhibition term be $k_{10}[O_2][N_2][X_O]$, then k_{10} may be evaluated in the following way. Inserting this term in the equation for X_O in addition to the term required by case three (oxygen initiation)

$$-\frac{d[PH_3]}{dt}=\frac{k[PH_3]I_n\cdot A}{[O_2]\{k_6[O_2]+k_{10}[N_2]\}}.$$

Hence

$$(1/R)/(1/R_0)=1+k_{10}[N_2]/k_6[O_2], \quad (28)$$

where the subscript $_0$ refers to the runs made in absence of foreign gas. From this equation the values of k_{10}/k_6 have been calculated and are given in Tables IV and V. Argon and nitrogen are about as efficient as oxygen in promoting the stability of the complex.

The next question is to determine the absolute values of k_6 and also of A. For this purpose, the ratio of the rates of oxidation to the rate of decomposition for the photosensitized and for the direct reaction were measured. The data are collected in Table VII.

Some notes about experimental procedure may be mentioned here. Since the ratio of the rates was large, the rate of decomposition was measured by a McLeod gauge and a filter was employed to cut down the intensity of the light during the oxidation experiments. In the direct reaction, comparison was made directly on the oil

TABLE VII. *Photosensitized experiments.*

p_{PH_3}	p_{O_2}	$d[PH_3]/dt$	Ratio of rates	Chain length (ν)	ν for 5 mm PH_3 and 50 mm O_2
		Above the upper limit			
1.98	37.5	0.93×10^{-2} mm/min. in 85 cc I 0.15	19.2	38	53
2.00	—	5.3×10^{-4} mm/min. in 514 cc I 1.00			
8.0	81.0	3×10^{-2} mm/min. in 85 cc I 0.15	10.4	21	34
8.0	—	3.2×10^{-3} mm/min. in 514 cc I 1.00			
6.8	68	8.4×10^{-2} mm/min. in 85 cc I 0.15	8.4	17	43
6.7	—	11×10^{-3} mm/min. in 514 cc I 1.00			
		Below the lower limit			ν for 0.5 mm PH_3 0.5 O_2
0.85	0.36	67×10^{-2} mm/min. in 85 cc I 0.15	480	10	820
0.79	—	0.93×10^{-2} mm/min. in 514 cc I 1.00			
0.83	—	0.93×10^{-2} mm/min. in 514 cc I 1.00	504	10	830
0.83	0.36	2.52×10^{-2} mm/min. in 85 cc I 0.0054			

At the lower limit explosion occurred with 0.83 mm PH_3 and 0.45 mm O_2.

Direct reaction

p_{PH_3}	p_{O_2}	Rate*	Chain length (ν)	ν for 0.5 mm PH_3 and 0.5 mm O_2
		Below the lower limit		
0.254	—	0.075	310	1200
0.254	0.337	11.6		
0.267	—	0.070	400	800
0.254	0.513	14.0		
		Above the upper limit		
8.23	121.4	54.0	72	210
8.64	—	1.5		
8.35	138.1	38.8	47	220
8.40	—	1.65		

* Multiply by 1.27×10^{-2} to give mm/min.

manometer. The rate of decomposition of phosphine was determined by measuring the pressure of hydrogen after the phosphine had been condensed out by liquid air. The ratio of the rates is doubled to give the chain length, for the quantum yield of the dissociation is 0.5.

First of all, it will be seen that, below the lower limit, the chain lengths for the direct and photosensitized experiments are nearly the same. Above the upper limit, however, the chain length (calculated from the relative velocities) in the direct reaction is about five times that obtained in the sensitized oxidation. This confirms the kinetic results about initiation by oxygen and moreover gives the value of A, the number of chains started per excited Hg atom deactivated by oxygen; it is 0.2. The kinetic experiments also yield information about the nature of initiation by oxygen. There is some doubt as to the products of reaction when a $^3P_1$ Hg atom collides with an oxygen molecule. If the low efficiency of initiation were due to the deactivation, by

collision or by radiation, of an excited oxygen molecule of very short life and if initiation be brought about by collision of this excited molecule with phosphine, then it may easily be shown that the initiation factor will assume the form $[PH_3]/[O_2]$ and hence the kinetic equation would become

$$-d[PH_3]/dt = \text{const. } [PH_3]^2/[O_2]^3,$$

which does not agree with experiment. Some atom or molecule must emerge from the collision which is not subject to such easy removal as an excited O_2 molecule; the most probable reaction is

$$Hg\ (^3P_1)+O_2 \rightarrow HgO+O,$$

the O atom reacting with the first PH_3 molecule it encounters.

One of the consequences of the theory of branched chains is that the explosion limit curve is a line of equal chain length. Therefore if the chain length be calculated below the lower limit and above the upper limit, and the results extrapolated to these limits employing the appropriate equations, then similar values should be obtained. Such a calculation has been made and the results are given in the last column of Table VII. Although the values of ν are of the same order of magnitude, it must be pointed out that at the upper limit, the chain length is five times shorter than at the lower limit.

The chain length measurements above the upper limit provide the material for a calculation of k_6. From the equation already given, the chain length is represented by

$$\nu = \frac{-d[PH_3]/dt\ (\text{oxidation})}{-d[PH_3]/dt\ (\text{decomp.})} = \frac{k[PH_3]}{k_6[O_2]^2}.$$

Substituting from Table VII, $\nu=200$, $[PH_3]=8.4$ and $[O_2]=138.1$ mm $k/k_6[O_2]=3300$. Since the propagation collisions are nearly 100 percent efficient, 3300 represents the ratio of the number of bimolecular to trimolecular collisions at 146 mm. Now it is generally assumed that at atmospheric pressure this ratio is 10^3, at 146 mm, it will be $760/146\times10^3=5200$ and therefore every second ternary collision is effective in destroying X_O. This result may be arrived at in another way. If the kinetics of the stable reaction and of the explosion are exactly similar, then from the above analysis the corresponding equation for the upper limit may easily be deduced by placing the probability of branching $(\alpha-1)$ in the equations for the stationary concentration of the carriers

$$d[X_O]/dt = I+\alpha k[X_P][O_2] - k[X_O][PH_3]-k_6[X_O][O_2]^2=0,$$

$$[dX_P]/dt = k[X_O][PH_3]+k[X_P][O_2]=0,$$

therefore

$$[X_O] = I/\{(1-\alpha)k[PH_3]+k_6[O_2]^2\}. \quad (29)$$

The condition for explosion is that

$$(\alpha-1)k[PH_3] = k_6[O_2]^2, \quad (30)$$

which is exactly in agreement with Dalton's experiments except at high phosphine pressures and also with experiments made during this investigation. To calculate $k/k_6[O_2]$, it is necessary to know $(\alpha-1)$. The chain length is 10^3 at the lower and 2×10^2 at the upper limit, the probability of branching is, respectively, 10^{-3} and 5×10^{-3}. At the upper limit, 5 mm PH_3 and 50 mm O_2, $k/k_6[O_2]$ is 10^4 and 2×10^3. At 55 mm, the ratio of bi- to trimolecular collisions is 1.5×10^4. The agreement is not quite so good with $(\alpha-1)$ obtained from the upper limit results.

A third method, however, obviates the necessity of determining $(\alpha-1)$ and k. At the lower limit

$$(\alpha-1)k[PH_3] = K/[O_2] \quad (31)$$

and at the upper limit

$$(\alpha-1)k[PH_3] = k_6[O_2]^2 \quad (32)$$

or

$$K/[O_2]^3 = k_6, \quad (33)$$

K can be calculated from the dimensions of the reaction tube and mean free path of the chain carriers in the gas. k_6 may then be evaluated and from it the efficiency of the trimolecular collisions. Semenoff[10] has made the calculations using Dalton's results and finds that 0.4 ternary collisions are effective.

Another check on the interrelationships between the stable and explosive reaction can be

[10] Semenoff, Phys. Zeits. d. Sow. 4, 714 (1934).

made. The whole explosion curve may be represented by the equation

$$(\alpha-1)k[PH_3]=K/[O_2]+k_6[O_2]^2, \quad (34)$$

obtained on adding (31) and (32). For $[PH_3]$ to be a minimum, then by differentiating (34) with respect to $[O_2]$.

$$[O_2]=3(K/2k_6)^{\frac{1}{3}}. \quad (35)$$

From the results shown in Fig. 4, the minimum occurs at 4.6 mm O_2. Similarly, ν below and above the limit is given by

$$\left.\begin{aligned}\nu_{\text{lower}}&=k/K\cdot[PH_3][O_2],\\ \nu_{\text{upper}}&=k[PH_3]/k_6[O_2]^2\end{aligned}\right\} \quad (36)$$

or

$$\nu=k[PH_3]([O_2]/K+1/k_6[O_2]^2).$$

Hence

$$d\nu/d[O_2]=k/K\cdot[PH_3]-2k[PH_3]/k_6[O_2]^3=0$$

or

$$[O_2]=(K/2k_6)^{\frac{1}{3}}$$

is the condition for the chain length to be maximum. Thus the maximum in the chain length curve should occur at the same oxygen pressure as the minimum in the explosion curve. Fig. 4 shows that these anticipations are realized. In the figure of the preliminary notice of this work,[11] the rate of reaction was plotted against the pressure of the oxygen, but it was also pointed out that the curve would have to be suitably corrected for deactivation of the mercury atoms by oxygen. On account of initiation by oxygen, however, the corrections to be made are small, so that the curve does represent the variation of chain length with oxygen pressure. This is more easily seen from Table VIII where the expression, $Z=[PH_3]+0.5A[O_2]/\{[PH_3]+0.5[O_2]+37\}$ is evaluated for different oxygen pressures.

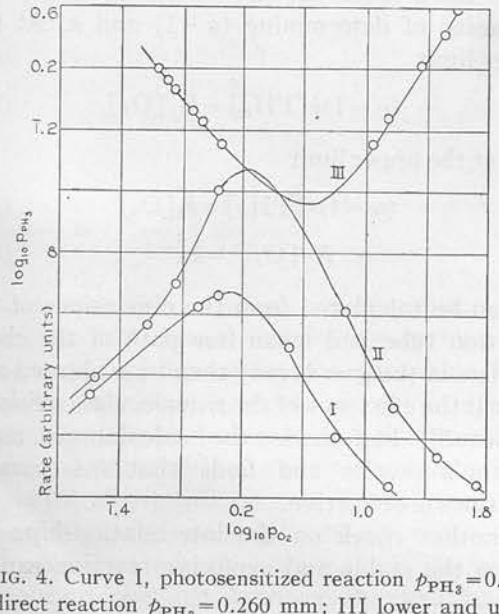

FIG. 4. Curve I, photosensitized reaction $p_{PH_3}=0.130$; II direct reaction $p_{PH_3}=0.260$ mm; III lower and upper limit, thermal explosion.

TABLE VIII. *Variation of initiation factor with oxygen pressure.* $[PH_3]=0.1$ mm

$[O_2]$	0.05	0.1	0.2	0.5	1.0	2.0	5.0	10.0	50.0
Z	0.20	0.21	0.21	0.21	0.21	0.20	0.20	0.20	0.20

The photosensitized results are also plotted in Fig. 4. The position of the minimum in the explosion curve, which is 0.212 mm PH_3 and 4.62 O_2, was calculated from Eq. (34).

EFFECT OF RATE OF STARTING OF THE CHAINS ON THE POSITION OF THE LIMITS

Excepting for the moment the oxidation of phosphorus and of phosphine, there is abundant evidence that the position of both limits is dependent on the rate at which chains are started. In the hydrogen-oxygen reaction, for example, it has been established that hydrogen atoms produced photochemically,[12] thermally[13] and electrically,[14] oxygen atoms[14] and chlorine atoms[15] all reduce the ignition temperature. Moreover, even at room temperatures, conditions simulating the lower limit may be obtained with spark ignition.[16] The action of nitrogen peroxide in reducing the temperature of ignition of hydrogen, carbon monoxide, methane, etc., may also be a question of the rate of starting affecting the limits. Similarly, the limits in the oxidation of

[11] Nature **131**, 690 (1933).
[12] Farkas, Haber and Harteck, Zeits. f. Elektrochemie **36**, 711 (1930); Taylor and Salley, J. Am. Chem. Soc. **55**, 96 (1933).
[13] Haber and Oppenheimer, Zeits. f. physik. Chemie **B16**, 443 (1932).
[14] Semenoff, Trans. Faraday Soc. **29**, 606 (1933); Phys. Zeits. d. Sow. **4**, 753 (1934).
[15] Norrish, Proc. Roy. Soc. **A135**, 334 (1931).
[16] Thompson, Trans. Faraday Soc. **28**, 308 (1932).

sulphur,[17] carbon disulphide[18] and hydrogen sulphide are considerably altered by suitable stimuli. Examples may be easily multiplied, but the situation can be summarized by the statement that, in those reactions where the limits are temperature dependent and where explosion occurs at elevated temperatures, the position of both limits is dependent *to some extent* on the rate of initiation. The chain hypothesis alone does not therefore wholly express the condition for explosion, in addition, some temperature dependent factor must be introduced to provide an adequate explanation for the phenomena. With phosphorus and phosphine, it is different, the propagating collisions are almost 100 percent efficient and the efficiency is so high that it cannot be dependent on temperature to any important degree. Similarly, the termination reactions at the walls and in the gas phase do not require activation. In these two examples, then, it is to be expected that the pure chain explosion would occur, and that the condition for explosion would be adequately expressed by the statement that the product of the probabilities of termination and of branching is equal to unity, from which it at once follows that the explosion pressure should be quite independent of the rate of starting. The test is rather a crucial one for some parts of the chain theory. Some time ago, it was applied to the lower limit of phosphine[19] and a very considerable lowering of the limit was obtained. The curious fact was that the effect persisted for a time much longer than the life of the reaction chains. Later it was shown[20] to be due wholly to an alteration of the surface upon which the chains terminated. In the experiments to be described below, the experiment has been repeated at the upper limit which is, of course, unaffected by wall conditions (more strictly the termination reaction only). Initiation was effected by the light from the mercury lamp (water-cooled).

Some indication of the behavior to be expected has already been given, since it has been shown that the chain lengths at the lower and upper limit are not identical. Apparently the explosion can occur more easily at high pressures in that such a long chain is not necessary.

Preliminary experiments showed at once that there was a considerable displacement of the upper limit to higher pressures, provided the tube was illuminated during expansion. Several experiments were carried out in which the gases were illuminated for a considerable time (min.) and allowed to stand for intervals of from 0.5 to 10 min. before expansion, but no displacement could be detected. Table IX contains a number of typical results.

TABLE IX.

Expt. No.	Initial press. p_{PH_3}	Initial press. p_{O_2}	Total press. at explosion	Conditions of illumination
561	6.5	103	72	during expansion
562	6.4	99	26	none
563	6.6	99.5	26	see text
565	5.3	103	57.3	during expansion
566	6.4	112	65	" "
567	4.7	95	56.5	" "

Expt. No.	Initial press. p_{PH_3}	Initial press. p_{O_2}	Total press. at explosion	Intensity
570	7.5	113	63.5	1.00
571	7.5	113	43.5	0.15
572	6.5	100	38.5	0.15
574	7.4	100	56.5	0.15
575	7.3	106	63.5	1.00
577	4.8	111	42.3	1.00
578	8.1	101	80.0	1.00

* Rate of stable reaction at initial pressure 0.13 mm/min., $I = 1.00$.

Experiments 561 to 563 may be particularly mentioned. The initial pressures were all practically the same, but the explosion pressure has been increased by illumination from 26 to 72 mm. In experiment 563 illumination was continued during expansion until the pressure was only 2 mm above the upper limit (72), the light was cut off and the expansion continued, but the pressure had to be reduced to 26 mm to obtain explosion. The time for the pressure to fall 2 mm was not more than 2 sec. so that the lifetime of the effect cannot exceed 2 sec. It is therefore quite different from the lower limit phenomenon which persists for several minutes. The effect of intensity was further investigated in the following way. Instead of plotting upper limit curves for different intensities two mixtures of constant composition were employed. Since expansion does not alter the composition, the displacement of the ex-

[17] Semenoff and Rjabinin, Zeits. f. physik. Chemie **B1**, 192 (1928).
[18] Ritchie and others, Proc. Roy. Soc. **A137**, 511 (1932).
[19] Clusius and Hinshelwood, Proc. Roy. Soc. **A129**, 589 (1930).
[20] Melville, Proc. Roy. Soc. **A138**, 389 (1932).

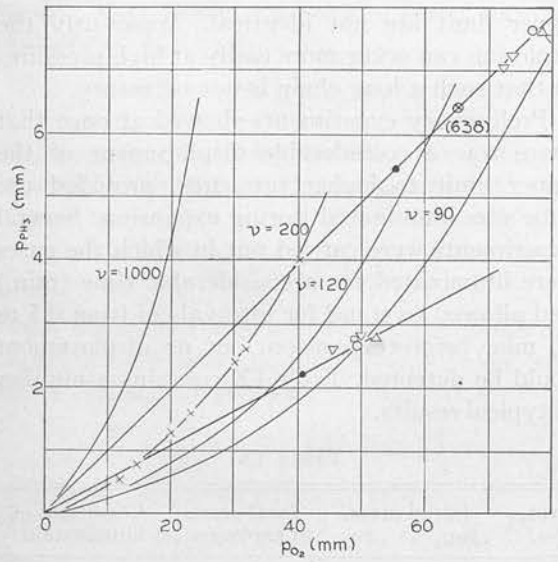

FIG. 5. Displacement of upper limit by illumination. Rate, ●≡5×10^{-5} mm/sec. (2.0×10^{10} quanta per sec.) ⊕≡10^{-4}, ⊙≡1.7×10^{-4}, △≡3.3×10^{-4}, □≡5.4×10^{-4}, ▽≡37×10^{-4}.

plosion limit along the expansion line can be regarded as a measure of the effect. The data are plotted in Fig. 5.

The intensity could not be increased to higher values since the velocity of the reaction was then sufficient to remove considerable amounts of phosphine and oxygen.

These results then prompt a further question as to whether, at the lower limit, in addition to the ordinary displacement owing to the change in surface, there is a transient effect similar to that at high pressures. The procedure adopted was to use a constant pressure of phosphine and allow oxygen to leak in through the needle valve and record the explosion pressure on the oil manometer. The intensity of the light was 0.15 on the same scale as that given in Table X. The results listed in Table X show the conditions of illumination and are recorded in the order in which the experiments were carried out.

Comparing Nos. 625, 626 and 633 with the remainder, it will be seen that the explosion pressures, in which there has been illumination, are somewhat lower than those in its absence, thus confirming previous results. It does not appear to matter whether the light is switched off sometime before the explosion or whether it is left on right up to the explosion limit. It will also

TABLE X. *Lower limit, silica surface.*

No.	p_{PH_3}	p_{O_2} at explosion	$p_{PH_3}+p_{O_2}$	Conditions of illumination
622	0.74	0.61	1.35	continuous
623	0.81	0.54	1.35	until $p_{PH_3+O_2}$ 1.26
624	0.80	0.49	1.29	" " 1.26
625	0.80	0.79	1.59	none
626	0.77	0.76	1.53	none
627	0.80	0.49	1.29	until $p_{PH_3+O_2}$ 1.26
628	0.78	0.48	1.26	continuous
629	0.76	0.44	1.20	until $p_{PH_3+O_2}$ 1.18
630	0.76	0.64	1.40	" " 1.12
631	0.76	0.48	1.24	" " 1.18
632	0.76	0.64	1.40	" " 1.12
633	0.77	0.74	1.51	none

be observed that if illumination be stopped at a low pressure of oxygen (expts. 630 and 632) the explosion limit is a little higher than that where illumination has been continued up to higher oxygen pressures. The conclusion then is that the transient effect, obtained at the upper limit, is not in evidence at the lower limit.

To demonstrate more clearly the sensitiveness of the upper limit to the stationary concentration of X_O, the following experiment (638) and calculations were made. A mixture of 12.0 mm. phosphine and 114 mm oxygen was prepared, illuminated during expansion when explosion occurred at 71 mm. Thus the intensity of the light was a somewhat greater (0.30) than 0.15 in the experiments in Table X, as is seen if the explosion point is placed on the upper expansion line of Fig. 5. A second mixture was then prepared and pumped down to 75 mm. At this pressure, the rate of oxidation of phosphine was 9.3×10^{-5} mm/sec. in a volume of 85 cc: the calculated chain length is 110. The number of quanta entering the reaction tube is thus 4×10^{10} sec^{-1}. At 75 mm, a molecule experiences about 10^6 ternary collisions per sec., or the interval between such collisions is 10^{-6} sec., which is therefore the mean life of X_O. The rate of production of X_O may be taken as the rate of dissociation of phosphine or $9.3\times10^{-5}/110$ mm/sec. $\doteqdot10^{-6}$ mm/sec. and the stationary concentration is thus 10^{-12} mm. According to Table X, when the stationary concentration of X_O attains 10^{-11} mm, the limit ceases to be affected. When such a small concentration of

carriers displaces the limit so much, it is not at all surprising that traces of water vapor and possibly other gases and also changes of temperature[9] exert a comparatively large influence. This, in turn, suggests that the displaced limit is really the true explosion limit and that the one observed in the thermal reaction is particularly low because of the fact that a sufficient number of chains do not start to fulfill the conditions required by the chain theory. If this were the case, the chain length at the displaced limit would be 10^3, whereas it is only 10^2. Both the probability of branching and of termination are processes involving the reaction of only one carrier and thus should be unaffected by variations in the concentration of that carrier.

The following theory may be advanced to account for these observations. As a result of a slow thermal reaction above the upper limit ozone is formed. Likewise in the stable photoreaction ozone is produced in much larger amounts as a consequence of the termination of the chains. Ozone increases the explosion pressure for every collision between X_P and O_3 gives rise to two X_O's, i.e., the probability of branching is increased. Ozone is destroyed by reaction with phosphine, but this is a comparatively inefficient reaction. In the photoreaction ozone is also decomposed photochemically. No chains are started, however, by these two processes. Expressing all these assumptions in the usual manner, the following equations are obtained

$$\left.\begin{aligned} d[O_3]/dt &= k_6[X_O][O_2]^2 - k[X_P][O_3] \\ &\quad - k_{10}I_0[O_3] - k_{11}[PH_3][O_3] = 0, \\ d[X_O]/dt &= I_T + I_P + \alpha k[X_P][O_2] \\ &\quad + 2k[X_P][O_3] - k[X_O][PH_3] \\ &\quad - k_6[X_O][O_2]^2 = 0, \\ d[X_P]/dt &= k[X_O][PH_3] - k[X_P][O_2] \\ &\quad - k[X_P][O_3] = 0, \end{aligned}\right\} \quad (37)$$

where I_0 is proportional to the intensity of the light decomposing the ozone, I_T and I_P are the thermal and photo rates at which chains are started. Solving and simplifying these equations, the condition for explosion is that

$$(\alpha-1)k[PH_3] + 2k[O_3]/[O_2] = k_6[O_2]^2, \quad (38)$$

from which it is evident that ozone facilitates explosion. The quantity required to exert a large effect is small. From Fig. 5, with 2 mm PH_3, the pressure of O_2 at the limit should theoretically be 12 mm; experimentally it is 26 mm and therefore if $(\alpha-1)=10^{-3}$ solution of (38) gives $[O_3]=10^{-2}$ mm. On solving (37) for $[O_3]$ above the explosion limit

$$[O_3] = (I_T + I_P)/(I_T + I_P + k_{11}[PH_3]),$$

which shows at once that in the photo-experiments when $I_P \gg I_T$ and $k_{11}[PH_3]$, this expression is independent of intensity in agreement with observation. Moreover the displacement at high oxygen pressures should not be quite so much as at low pressures. Examination of Fig. 5 reveals that the explosion points on the upper expansion line lie somewhat to the left of the curve for $\nu=90$. At low values of I_P, $k_{11}[PH_3]$ comparable with I_P, the displacement of the limit will be proportional to the intensity. In order to preserve the form of the explosion curve for the dark reaction it is necessary to assume that $I_T \sim [PH_3][O_2]$ in which case the term containing $[O_3]$ becomes independent of phosphine and oxygen pressure.

On account of the sensitiveness of the upper limit to the stationary concentration of chain carriers, an attempt was made to measure the rate of the thermal reaction outside the explosion limits. For this purpose a quantum counter sensitive to radiation of $\lambda < 2800$A and capable of detecting 50 quanta per minute was employed.[21] Two mixtures were made up (a) below the lower limit, 0.396 mm PH_3 and 0.37 mm O_2, $\nu=250$, (b) above the upper limit 8.7 mm PH_3, 132 mm O_2, $\nu=50$, and the tubes placed in close proximity to the counter, but no radiation could be detected. It may of course be that there is reaction accompanied by radiation which does not affect the counter.

Elsewhere it has been suggested that oxidations brought by nitrous oxide instead of by oxygen cannot proceed explosively by branching chains, although straight chains are readily obtained. Experiments were therefore made with phosphine-nitrous oxide mixtures to see if chains could be started by the photodissociation of the phosphine, but no chain propagation occurred.

In view of these experiments and calculations,

[21] Ouellet, Trans. Faraday Soc. **29**, 486 (1933).

there are consequently good grounds, though the evidence is not direct, for supposing that X_O is an oxygen atom. Furthermore, it is possible that the collision which gives rise to branching is that between X_P and O_2, yielding two oxygen atoms.

The existence of an upper limit can be attributed to two causes (*a*) removal of the chain carriers by a reaction of higher order than that of branching, e.g., phosphine, (*b*) a deactivating influence of the reactants on a collision complex which would otherwise give rise to two chains, e.g. hydrogen, (*c*) other causes not at present included in the theory. It will be a matter for further experiment to decide, by closely examining the relationship between the kinetics of the stable and explosive reactions, which mode of deactivation causes the upper limit in other chain reactions. Such experiments may reveal whether, as in the case of phosphine, explosion occurs at the upper limit more readily than theory predicts.

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INERT GAS EFFECTS AT THE LOWER EXPLOSION LIMIT OF PHOSPHINE-OXYGEN MIXTURES

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By S. C. Gray and H. W. Melville.

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Recently a correlation between the kinetics of the stable chain oxidation and those of the explosion limits in phosphine-oxygen mixtures has been established.[1] The data above and at the upper explosion limit have shown conclusively that, in this reaction at least, one of the carriers is an oxygen atom and that the principal cause of termination of reaction chains in the gas phase is due to the triple collision

$$O + O_2 + M \rightarrow O_3 + M,$$

where M may be O_2, PH_3 or any inert gas present.

Furthermore, it would appear that nearly every such triple collision is effective in removing the oxygen atom. This mode of termination of the chains becomes of importance when the pressure of oxygen is greater than 4 mm. and indeed gives rise to the appearance of the upper limit.

At lower pressures, however, the chains end upon the walls of the reaction tube with the result that inert gases, which function as inhibitors at higher pressures, now act as accelerators by the well-known process of impeding the diffusion of the reaction centres to the walls. The quantitative theory of the effect has shown that the increase in chain length can be represented by the factor $(1 + \mu[X])/([PH_3] + [O_2])$ where μ is a constant dependent on the nature of the inert gas but independent of its pressure. The early results,[2] however, exhibit a distinct decrease in the value of μ as the pressure of the inert gas increases. Table I. shows some typical figures :—

TABLE I.

Nitrogen (Series D).				**Argon** (Series E.)			
$[O_2]$. mm.	$[PH_3]$. mm.	$[N_2]$. mm.	μ.	$[O_2]$.	$[PH_3]$.	[A].	μ.
0·85	0·61	—		1·05	0·70	—	—
0·82	0·59	0·54	1·82	0·84	0·56	0·51	1·54
0·68	0·49	1·68	0·39	0·70	0·51	1·11	1·03
0·64	0·46	3·24	0·26	0·69	0·46	1·59	0·96
				0·65	0·44	2·09	0·82
				0·67	0·45	2·86	0·63

This falling off in the magnitude of μ was attributed to gas phase inhibition without specifying its nature. From the data obtained at the upper limit, it is easy to show that gas phase inhibition should be

[1] Melville and Roxburgh, *J. Chem. Physics*, **2**, 739, 1934. Previous references to the kinetics of the reaction are given in this paper.

[2] Dalton and Hinshelwood, *Proc. Roy. Soc.*, **125A**, 294, 1929.

entirely negligible at the pressures employed at the lower limit. Using the same notation as before, the chain length with wall and gas termination is respectively given by

$$\nu_{wall} = k[PH_3][O_2]/K \,.\, \{1 + \mu[X]/([PH_3] + [O_2]\} \,. \quad . \quad (1)$$

$$\nu_{gas} = \frac{k[PH_3]}{k_6[O_2]([O_2] + [X])} \,. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where k is the velocity coefficient for the propagation reaction; K is the rate at which O atoms diffuse to the walls at a total pressure of 1 mm., k_6 is the velocity coefficient for the removal of O atoms in the ternary collision. From the position of the minimum in the explosion curve, which is at 4·62 mm. O_2 for a 2 cm. tube, it can be shown [1] that $\sqrt[3]{K/2k_6} = 4{\cdot}62$. In one experiment [2] in Series D (nitrogen) the value of μ fell to 0·26 when $[PH_3] = 0{\cdot}46$, $[O_2] = 0{\cdot}64$, $[N_2] = 3{\cdot}24$. The ratio gas to wall deactivation is given by

$$\frac{1/\nu_{gas}}{1/\nu_{wall}} = [O_2]/K\{1 + \mu[X]/([PH_3] + [O_2]\}k_6[O_2]([O_2] + [X] \,. \quad (3)$$

Taking $\mu = 0{\cdot}71$ (*vide infra*), and substituting the above values, this ratio is 0·025, so that at these pressures only 1/40 of the chains terminate in the gas phase.

Apart from this discrepancy, the remainder of the observations on the behaviour of the reaction appeared to be in so good agreement with theory as to warrant a repetition and extension of the earlier results on the effect of inert gases at the lower limit to make sure that there was no additional kind of gas phase deactivation to be included in the theoretical treatment.

Experimental.

Two methods were employed in determining the position of the lower limit. The first consisted in measuring the gases into the reaction vessel, compressing the mixture until it exploded, and from the original pressure and known volume change, calculating the pressure at the explosion point. In the second, the inert gas and phosphine were passed into the reaction tube, and oxygen allowed to enter slowly through a capillary until explosion took place. Of these methods the second proved much superior, since it yielded more consistent results.

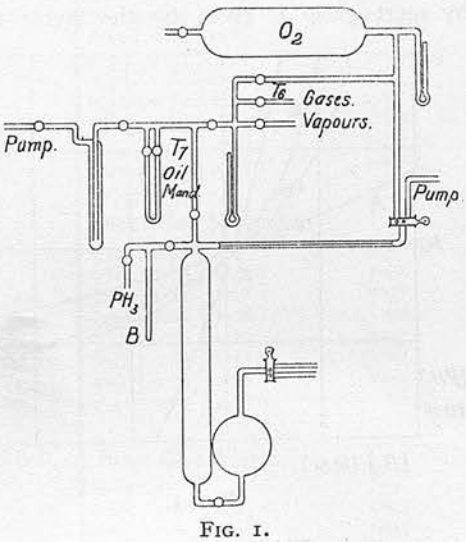

FIG. 1.

The principal part of the apparatus is shown in Fig. 1. Exhaustion was effected by a mercury condensation pump backed by an oil pump. Phosphine was stored in B and the various inert gases and organic liquids in separate reservoirs. Oxygen entered by the capillary at the end of which there was a two-

way tap for arresting the flow after the explosion. The procedure was (*a*) to raise and lower the mercury to wash the walls with phosphoric acid, (*b*) admit phosphine from B, its pressure being recorded on the oil manometer, (*c*) admit the inert gas by opening T_6. After a short interval to allow the gases to mix, T_7 was closed to avoid slight solution of the gases in the oil and oxygen admitted until there was explosion, the time of entry being noted by stop watch. The explosion pressure was then calculated by means of previous calibration experiments. The walls were again washed preparatory to carrying out the next explosion.

The following gases and vapours were employed : H_2, Ne, A, N_2, CO_2, N_2O, SO_2, $PbMe_4$, CCl_4, C_6H_6, C_2H_4.

The gases were prepared as described in previous papers. The neon contained 2 per cent. helium and the condensable gases were fractionated with liquid air as were the liquids. The benzene and carbon tetrachloride were free from sulphur. The lead tetramethyl was prepared in the following way.

Twenty-four gm. magnesium foil, dried in a steam oven were placed in a 1-litre flask, and covered with 400 c.c. absolute ether, dried over sodium and redistilled. A reflux condenser fitted with a calcium chloride tube was attached and 142 gm. methyl iodide added in small quantities through the condenser. The flask was removed from the water bath and 125 gm. lead chloride added in small portions through the condenser. The mixture was heated for a few minutes, cooled to 0° C. and the magnesium compound decomposed by the addition of 200 c.c. water, the mixture being finally heated to complete the reaction. The contents of the flask were filtered through cotton wool into a separating funnel and the aqueous layer run off. The ethereal layer was dried over calcium chloride and the ether removed. The residue was transferred to a small distilling flask and redistilled several times, the fraction passing over at 108-110° being collected. Distillation was continued until no residue was left in the distilling flask. Yield of purified product 30-40 gram.

Discussion of Results.

It has been mentioned previously that the acceleration brought about by inert gases is given by the factor $1 + \mu[X]/([PH_3 + O_2])$. The calculation of μ is thus dependent on the accuracy with which this relationship holds, two simplifying assumptions being made in its deduction, namely that the two carriers X_O and X_P react equally readily with phosphine and oxygen respectively, and are destroyed on impact with the walls at similar velocities. This naturally gives rise to the symmetrical formula for the explosion limit $[PH_3][O_2] = \text{const.}$ If, however, X_O reacts more rapidly with PH_3 than X_P with O_2, then it can be shown that the explosion limit is given by $[O_2]\{[PH_3] + [O_2]\} = \text{const.}$, whereas if X_P reacts

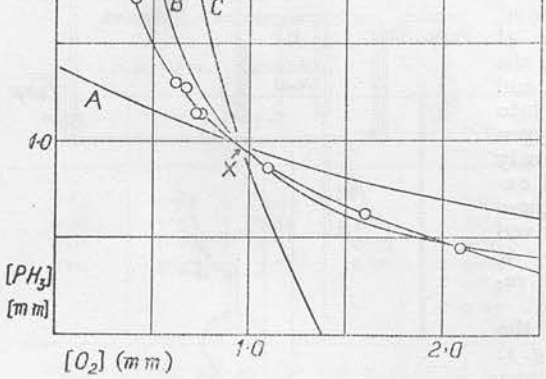

FIG. 2.

more quickly $[PH_3]\{[PH_3] + [O_2]\} = \text{const.}$ A series of typical results has therefore been plotted in Fig. 2. Three curves have been drawn through the point X, the intersection of the line drawn at 45° to the $[O_2]$ axis and the explosion curve, *viz.*,

(A) . . . $[O_2]\{[PH_3] + [O_2]\} = 1{\cdot}80$;
(B) . . . $[PH_3][O_2] = 0{\cdot}90$;
(C) . . . $[PH_3]\{[PH_3] + [O_2]\} = 1{\cdot}80$,

from which it will be seen that the symmetrical equation conforms most closely with experiment.

Some typical results are given in Tables II. and III. In the last column $[PH_3][O_2]\{1 + [X]/[PH_3] + [O_2]\}$ has been calculated to demonstrate that this product remains constant up to high inert gas pressures and also to indicate the consistency in the explosion pressures. Such consistency could not be attained in the compression method. The series of experiments,

TABLE II.

$[PH_3]$.	$[O_2]$.	[X].
Inert Gas Hydrogen.		
0·66	1·36	—
0·65	1·38	0·23
0·65	1·39	0·65
0·66	1·36	1·10
0·66	1·38	1·42
0·65	1·34	0·86
0·64	1·41	—

TABLE III.

$[PH_3]$.	$[O_2]$.	[X].	$[PH_3][O_2]\left\{1+\frac{[X]}{[PH_3]+[O_2]}\right\}$.	$[PH_3]$.	$[O_2]$.	[X].	$[PH_3][O]_2\left\{1+\frac{[X]}{[PH_3]+[O_2]}\right\}$.
Inert Gas SO_2.				**Inert Gas CO_2.**			
0·64	1·05	0·22	0·76	0·66	1·38	—	—
0·59	0·78	0·63	0·68	0·71	1·18	0·22	0·94
0·55	0·55	1·06	0·60	0·62	1·14	0·43	0·88
0·40	0·54	1·52	0·78	0·59	0·95	0·88	0·83
0·43	0·61	1·29	0·58	0·50	0·87	1·08	0·90
0·53	0·75	0·86	—	0·56	0·81	1·26	0·89
0·64	1·34	—	—	0·54	0·77	1·52	0·91
				0·45	0·71	1·95	0·88
				0·43	0·57	2·63	0·88
				0·32	0·61	3·23	0·88
Inert Gas N_2O.				**Inert Gas Nitrogen.**			
0·64	1·34	—	—	0·64	1·38	—	—
0·64	1·20	0·44	0·95	0·65	1·15	0·43	1·02
0·62	1·07	0·65	0·91	0·62	1·12	0·68	0·97
0·58	1·00	0·88	0·91	0·58	1·02	1·08	1·00
0·55	0·99	1·08	0·93	0·58	0·96	1·29	1·03
0·53	0·92	1·30	0·93	0·57	0·83	1·73	1·05
0·49	0·90	1·54	0·94	0·51	0·74	2·36	1·09
0·31	0·87	2·77	0·90	0·43	0·73	3·03	1·12
0·39	0·79	2·28	0·91				
Inert Gas Neon.				**Inert Gas Argon.**			
0·66	1·41	—	—	0·60	1·48	—	—
0·63	1·34	0·23	0·95	0·63	1·19	0·45	0·94
0·61	1·26	0·69	0·94	0·63	1·10	0·64	0·95
0·57	1·21	1·07	1·10	0·60	1·07	0·86	0·98
0·52	1·12	1·52	1·11	0·58	1·05	1·07	1·01
0·57	1·26	0·88	1·07	0·57	0·96	1·30	1·02
				0·56	0·90	1·56	1·03

carried out at different stages in the investigation, show the degree of concordance among the runs:

Nitrogen . .	$\mu = 0{\cdot}72$	0·73	0·68	0·72	0·69	0·73	0·70
Neon . .	$\mu = 0{\cdot}52$	0·52	0·51	0·55	0·52	0·55	0·52

The value of the inert gas coefficient μ for each gas is given in Table IV., each being the mean of several runs. The quantity $1/[PH_3][O_2]$ has been plotted against $1 + [X]/([PH_3] + [O_2])$ in Fig. 3. It will be observed that there is no tendency for the lines to curve round at the highest inert gas pressures used in these experiments, although if much higher pressures had been employed such a curvature would be observed having its origin in the type of collision responsible for the existence of the upper limit. The effect of sulphur dioxide is somewhat greater than that anticipated on the diffusion theory, and consequently great care was taken in its fractionation, but repetition of the experiments yielded exactly the same value of μ.

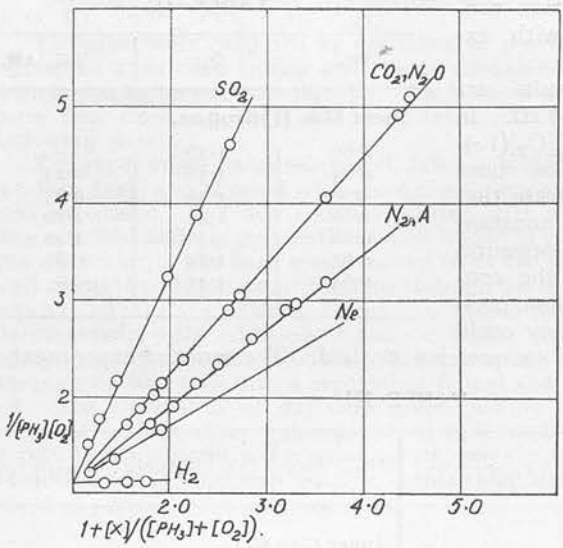

FIG. 3.

Shortly after the diffusion effect was noticed, a table of inert gas coefficients was compiled from the results then available.[3] This table can now be considerably extended to demonstrate how nearly all the results fit in with theoretical expectations. Taking the hydrogen-oxygen first, it will be seen that the μ's from the thermal and spark lower limit agree fairly well, and, moreover, occupy their expected place in the horizontal column of the table in that μ decreases from $H_2 - O_2$ to $P_4 - O_2$. The values obtained above the upper limit from the stable reaction appear to be somewhat high, which would suggest that, in addition to impeding diffusion, these gases may play some part in facilitating initiation of chains.

Of considerable interest is the comparison between the oxidation of phosphine and the thermal decomposition of ozone. First it is necessary to explain how μ is determined for ozone, since the calculation is not so straightforward as in the case with the other reactions.

Under suitable conditions [6] ozone decomposes according to the following scheme:—

$$\begin{aligned} O_3 &\rightarrow O_2 + O \quad k_1 \text{ (pseudo-unimolecular)},\\ O + O_3 &\rightarrow 2O_2 \quad k_2\\ O &\rightarrow \tfrac{1}{2}O_2 \quad K \text{ (wall reaction)}, \end{aligned}$$

[3] Melville, *Trans. Faraday Soc.*, **28**, 814, 1932.

TABLE IV.—Reaction and Origin of Results.

Inert Gas.	$H_2 - O_2$,[4] Lower Limit Thermal.	$H_2 - O_2$, Lower Limit Spark.	$H_2 - O_2$, Above Upper Limit.	$CH_4 - O_2$, Lower Limit Spark.
H_2 . .	—	—	—	—
He . .	0·30	0·15	2·3	—
Ne . .	—	—	—	—
N_2 . .	1·10	2·35	5·1	1·2
A . .	0·9	1·16	7·3	0·8
O_2 . .	—	—	—	—
CO_2 . .	0·39	2·4	—	1·5
N_2O . .	—	4·8	—	—
SO_2 . .	—	2·6	—	2·7
CCl_4 . .	—	5·6	—	3·4
$CHCl_3$ . .	—	6·9	—	3·0

TABLE IV. (*continued*).

Inert Gas.	$PH_3 - O_2$,[5] Lower Limit.	O_3,[6] Thermal Decomp.	$H_2S - O_2$, Lower Limit, Filament.	$CS_2 - O_2$, Lower Limit, Filament.	$CO - O_2$[7], Lower Limit, Thermal.	$H_2 - Br_2$,[8] Photo Synthesis.	$P_4 - O_2$, Lower Limit.
H_2 .	<0·1	0·21 *	—	—	—	0·09	0·10
He .	—	0·23	—	—	—	0·20	0·13
Ne .	0·52	0·47 *	—	—	—	—	0·20
N_2 .	0·71	0·73	0·44	0·42	0·6	1·03	0·37
A .	0·77	0·83	0·59	0·64	1·2	—	0·46
O_2 .	—	0·71	—	—	—	1·03	—
CO_2 .	1·04	0·82 *	—	0·83	—	1·25	0·48
N_2O .	1·04	0·82 *	—	—	—	—	0·46
SO_2 .	—	0·96 *	—	0·92	—	—	0·52
CCl_4 .	—	1·72 *	—	—	—	4·30	0·84
$CHCl_3$.	—	—	—	—	—	—	0·84

* Calculated.

which yields

$$-\frac{d[O_3]}{dt} = k_1[O_3]\left\{1 + \frac{k_2[O_3]}{k_2[O_3] + K}\right\} \quad . \quad . \quad (4)$$

k_1, k_2 and K are velocity coefficients. K is proportional to $(1/D_{O_3} + 1/D_X)^{-1}$ where D_{O_3} and D_X represent the diffusion coefficients of O atoms through ozone and the inert gas respectively. μ is defined by the equation

$$R_X/R_0 = 1 + \mu[X]/[O_3] \quad . \quad . \quad . \quad . \quad (5)$$

where R_X/R_0 is the relative increase in velocity of that process which is affected by wall deactivation when inert gas is added. But

$$R_X/R_0 = \frac{K(\text{in absence of X})}{K(\text{in presence of X})} = \frac{1/D_{O_3} + 1/D_X}{1/D_{O_3}} = 1 + D_{O_3}/D_{O_2} \quad (6)$$

therefore from the observed increase in the rate of ozone decomposition and the above kinetic equation, the two values of K may be readily

[4] Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.*, **138A**, 311, 1932.
[5] Present investigation.
[6] M. Ritchie, *Proc. Roy. Soc.*, **146A**, 848, 1934.
[7] Hadman, Thompson and Hinshelwood, *Proc. Roy. Soc.*, **138A**, 297, 1932.
[8] M. Ritchie, *Proc. Roy. Soc.*, **146A**, 828, 1934.

calculated. Since $D_{O_3} = \frac{\text{const.}}{\sigma^2_{O-O_3}}(1M/o + 1/M_{O_3})^{\frac{1}{2}}[O_3]^{-1}$, where σ_{O-O_3} is the sum of the radii of O and O_3, then μ is given by

$$\mu = \frac{1/\sigma^2_{O-O_3}(1/M_O + 1/M_{O_3})^{\frac{1}{2}}}{1/\sigma^2_{O-X}(1/M_O + 1M_X)^{\frac{1}{2}}} \quad . \quad . \quad . \quad (7)$$

The value of μ thus computed is in excellent agreement with experiment, and justifies the calculation of μ for other gases, although these have not yet been measured.

The concordance in the values of μ for the phosphine and ozone reactions is so close that it provides further reliable evidence that the oxygen atom is one of the carriers in the former reaction. The carbon monoxide results are subject to some uncertainty for the explosion curve is not represented accurately by a rectangular hyperbola. One important point may be mentioned about the $H_2 - Br_2$ results, and it applies in a modified degree to the $H_2 - O_2$ reaction. In the rigorous theory of the diffusion effect, account should be taken of the fact that the carriers do not diffuse through the reactants at the same speeds—the diffusion coefficient of bromine atoms through hydrogen is 8·4 times greater than that through bromine vapour at the same pressure. The value of μ will consequently be dependent on the composition of the mixture, increasing with the percentage of hydrogen. This is the reason for μ being so large in the H_2—Br_2 reaction, since $[H_2] = 200$, $[Br_2] = 15$ and $[HBr] = 4{\cdot}5$. If equimolecular mixtures had been employed, the value of μ would have been much smaller, thus falling into line with the other reactions given in the table.

Inhibition at the Lower Limit.

In marked contrast to the behaviour of the simple inert gases, ethylene, benzene, carbon tetrachloride, and lead tetramethyl raise the lower limit when added in relatively small quantities (Table V.). Moreover, it is noteworthy that these molecules all lower the explosion limit of $P_4 - O_2$ mixtures. At first, it would appear that a strange anomaly exists between the two reactions, in other respects so exactly similar, but a simple explanation is obvious when the problem is treated in the following way. It will be assumed that inhibition at these low pressures is due to the removal of oxygen atoms, X_O, by the foreign gas or vapour and that the rate of the reaction is $k'[X_O][X]$. The stationary concentration of X_O is thus reduced, and the expression for $[X_O]$ becomes

$$\frac{d[X_O]}{dt} = I + k[X_P][O_2] - k[X_O][PH_3] - K[X_O] - k'[X_O][X] = 0 \quad (8)$$

I being the rate at which X_O is produced spontaneously in the explosive reaction and photochemically in the stable reaction. $[X_P]$ is not affected, therefore

$$\frac{d[X_P]}{dt} = k[X_O][PH_3] - k[X_P][O_2] - K[X_P] = 0 \quad . \quad (9)$$

On solving these equations and simplifying on the assumption that the chains are long.

$$-\frac{d[PH_3]}{dt} = \frac{Ik[PH_3]/K'}{1 + k'[X]/K' + [PH_3]/[O_2]} \quad . \quad . \quad (10)$$

TABLE V.

Foreign Gas.	$[PH_3]$.	$[O_2]$.	[X].	k'/k.
CCl_4 . . .	0·67	1·41	—	—
	0·65	2·71	0·20	$1·5 \times 10^{-3}$
	0·66	1·40	—	—
$PbMe_4$ . . .	1·28	0·89	—	—
	1·29	1·59	0·11	5×10^{-3}
	1·48	2·00	0·22	$3·6 \times 10^{-3}$
	1·77	2·62	0·32	$3·1 \times 10^{-3}$
C_6H_6 . . .	1·27	0·87	—	—
	1·30	1·07	0·11	$2·4 \times 10^{-3}$
	1·29	0·86	—	—
	1·30	1·04	0·09	$2·3 \times 10^{-3}$
	1·32	2·21	0·32	$2·5 \times 10^{-3}$
	1·33	1·38	0·21	$2·3 \times 10^{-3}$
C_2H_4 . . .	0·65	1·44	—	—
	0·64	1·70	0·106	$0·8 \times 10^{-3}$
	0·65	1·82	0·125	$1·0 \times 10^{-3}$

Direct photo-oxidation, Zn spark.*

C_2H_4.	$[PH_3]$.	$[O_2]$.	$[C_2H_4]$.	$t_{\frac{1}{4}}$.	k'/k.
	0·461	0·866	—	27	—
	0·480	0·918	0·605	82	$0·9 \times 10^{-3}$
	0·271	0·502	—	46	—
	0·269	0·504	0·466	80	$0·7 \times 10^{-3}$

$t_{\frac{1}{4}}$ is the time in seconds for the reaction to go 25 per cent. to completion.

* The authors are indebted to Dr. H. L. Roxburgh for these data.

If R_0 and R be the rates in absence of and in presence of X, then

$$R_0/R_X = 1 + \frac{k'}{K}[X][O_2]\left(1 + \frac{\mu[X]}{[PH_3] + [O_2]}\right) . \quad . \quad (11)$$

where K is the value of K' at a total pressure of 1 mm. of PH_3 and O_2, μ is the inert gas coefficient for X. On substituting the appropriate values k'/k may be calculated. But ν, the chain length below the lower limit is given by $\nu = k/K[PH_3][O_2]$, k/K and k'/k may therefore be computed. If it is further assumed that the propagation collisions are 100 per cent. efficient, then the ratio k'/k gives the efficiency of the inhibition collisions directly.

In the explosive reaction account must be taken of branching and the equation for $[X_0]$ becomes

$$\frac{d[X_0]}{dt} = I + \alpha k[X_P][O_2] - k[X_0][PH_3] - K[X_0] - k'[X_0][X] = 0 \quad (12)$$

$(\alpha - 1)$ being the probability of branching. On solving these equations, equating the coefficients of terms containing $[X_0]$ to zero and carrying out the necessary simplifications, the explosion pressures are given by the equation

$$[O_2](k(\alpha - 1)[PH_3] - k'[X]) = K(1 + \mu[X]/([PH_3] + [O_2]) \quad . \quad (13)$$

It can now be seen why the oxidation of phosphine is much more sensitive to poisons than is the oxidation of phosphorus. Although the magnitude of the propagation coefficients are probably similar, the probability of

branching is widely different. For $P_4 - O_2$ ($\alpha - 1$) is about 10^{-1}, and[1] for $PH_3 - O_2$, 10^{-3}. If X_O in the phosphorus reaction is also an oxygen atom and therefore similar inhibitive processes are at work in the two reactions, then the phosphine reaction will be 100 times more sensitive to a given poison. It is therefore not surprising that benzene, ethylene, carbon tetrachloride behave as inert gases in the $P_4 - O_2$ reaction by lowering the limit, whereas they act as strong poisons in the $PH_3 - O_2$ reaction by raising the limit. By substituting the figures in Table III. in equation (13), the ratio k'/k has been evaluated for each gas, and is given in the last column of the table. The required values of μ were calculated by analogy with the other reactions listed in Table II. k'/k obtained for ethylene from the explosive data may be checked by measuring the retardation of the stable photochemically induced oxidation below the lower limit. Ethylene does not absorb the radiation of the zinc spark which is responsible for the dissociation of phosphine and thus no correction on this account need be applied. Again, it is a marked inhibitor although acceleration by inert gases (*e.g.*, argon) is also displayed in the same pressure range.[9] Employing equation (11), k/K has been evaluated, and as ν in the tube used was 800 for 0·50 mm. PH_3 and 0·50 mm. O_2, $k/K = 3200$, k'/k is given in the last column. The agreement between the values is exceedingly good considering the different nature of the two reactions. Relatively the stable reaction is less sensitive to poisons because the chain length is shorter than that at the explosion limit, the determination of k' is thus more accurate. This method is, of course, limited by the fact that most of the inhibitors absorb light of longer wave-length than phosphine itself.

The relative, and on certain suppositions the absolute, values of the inhibition coefficients for the $P_4 - O_2$ reaction can be obtained from their influence on the upper limit.[10] If the two reactions are really identical in that X_O is an oxygen atom, it would be expected that at least the relative values of k' would be identical. Such is apparently not the case. For $P_4 - O_2$, benzene and sulphur dioxide are both weak inhibitors, whereas for $PH_3 - O_2$, the latter behaves as an inert gas and the former as an inhibitor. Similarly, ethylene is ten times more powerful than benzene in $P_4 - O_2$, but exerts about the same effect on $PH_3 - O_2$. Lead tetramethyl is a comparatively weak inhibitor for $PH_3 - O_2$, contrasting with the powerful inhibitive action of lead tetraethyl[10] in $P_4 - O_2$. There are, unfortunately, no data at the upper limit of $PH_3 - O_2$ mixtures to check the magnitude of the inhibition observed at the lower limit.

The authors are greatly indebted to Dr. E. B. Ludlam for his ready encouragement throughout the work, and to Professor E. K. Rideal for kindly criticism of the manuscript. One of them (H. W. M.) thanks the Royal Commissioners of the Exhibition of 1851 for a Senior Studentship, and the other the Trustees of the Moray Fund of Edinburgh University for a grant.

Summary.

The effect of foreign gases on the lower explosion limit of $PH_3 - O_2$ mixtures has been determined as accurately as the experimental conditions will permit. H_2, Ne, A, N_2, CO_2, N_2O, and SO_2 all lower the limit in the normal way by impeding the diffusion of the chains to the walls. There is

[9] Melville, *Proc. Roy. Soc.*, **138A**, 389, 1932.
[10] Melville, *Trans. Faraday Soc.*, **28**, 312, 1932.

no measurable gas phase inhibition when the pressure of the gas is of the same order as that of the phosphine and oxygen. This agrees with observations on the effect of some of these gases on the upper limit.

C_2H_4, C_6H_6, $PbMe_4$, and CCl_4 all raise the lower limit in marked contrast to the lowering of the limit observed with $P_4 - O_2$ mixtures. It is shown that the reason for the difference is that the probability of branching of chains in the $PH_3 - O_2$ reaction is less than that in $P_4 - O_2$ mixtures, and that a given inhibitor exerts a more powerful influence on the former reaction. The value of the inhibition coefficient has been calculated and in the case of ethylene, checked by measuring the inhibition of the stable photo oxidation of phosphine.

An extended table of inert gas coefficients has been compiled.

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